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EDITED BY A. A. HALL, M.Sc., PH.D.

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# UNIVERSITY OF DURHAM PHILOSOPHICAL SOCIETY.

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## SOME CUSTOMS OF THE TAWNGPENG PALAUNGS.

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By J. COGGIN BROWN, M.Sc., F.G.S.

[Read November 24th, 1910.]

Tawngpeng<sup>1</sup> is the smallest of the Northern Shan States of Upper Burma. It has an area of about 800 square miles grouped roughly around Namhsau, the capital of the state. This town lies approximately in lat. 23°, long. 97° 10'. The whole district consists of narrow, well defined mountain ridges, with steep sided and deep valleys between, and, unless under cultivation, is as a rule covered with dense jungle.<sup>2</sup> The Palaungs,<sup>3</sup> who form the very large majority of the inhabitants of the state, belong to the Mon Hkmer family of Indo-China, which also contains the head-hunting Was of the country east of the Salween River, and the K'amus who, with allied races, stretch down into Cambodia. It is probable that tribes of this family were the first Mongolian race to inhabit Indo-China, and it is remarkable that the Palaungs, left behind in the general southerly movement of the family, have preserved from the remote past so many of their national customs, their language, and their characteristic female dress; and, in spite of the later influx of Shan and Tibeto-Burman races, are ruled to-day by their own chief.

### NUMBERS.

There are supposed to be about 17,000 Palaungs in Tawngpeng, whilst at the Burma census of 1901, 56,566

<sup>1</sup> Burmese, Taung baing.

<sup>2</sup> For an outline of the geology of part of this area, see "The Silver-Lead Mines of Bawdwin, Northern Shan States," by T. D. La Touche, B.A., F.G.S., and J. Coggin Brown, B.Sc., F.G.S., F.C.S., *Recs. Geol. Sur. India*, vol. xxxvii., part 3, 1909, pp. 238-241.

<sup>3</sup> The term *Palaung* is of Burmese origin. The people call themselves *Ta-ang* or *Ra-ang* and *Ku-mai*. They are known to the Shans as *Koon loi* or hill men (Shan, *koon* = man, *loi* = hill), whilst the Yunnanese Chinese refer to them as Pong-long, which may be a corruption of the Burmese name.

Palaungs were returned from the enumerated tracts. The others are scattered over the hilly districts of the Northern Shan States of Hsipaw, North and South Hsenwi, and in Möngmit, a Shan State which is administered as a sub-division of the Ruby Mines District. There are other isolated villages both in this and the Bhamo districts, whilst they are found as far south as Keng-tung in the Southern Shan States. They extend eastwards into the Chinese Shan States, but are never found at any great distance from the frontier.

#### PERSONAL APPEARANCE AND CHARACTER.

The Palaungs are a short, well-built race, light brown in complexion, with straight black hair. The nose is wide at the base. They are sub-brachycephalic and prognathous.<sup>4</sup> The tribe is not a handsome one and a predilection for betel-chewing does not tend to enhance its personal appearance. Both men and women are to a certain extent industrious. They are very reserved and shy, and in comparison with the Shans, morose. I know of a village which was abandoned by its owners, owing to the proximity of a new cart road, which brought numbers of strangers near them. They are quiet and law-abiding, with none of the daring of the Chingpaw, whilst in religious matters they display considerable zeal, without the corybantic tendencies of some of their neighbours.

#### VILLAGES.

The villages are almost always situated in elevated positions and usually in the most inaccessible places at or near the top of steep ridges. The houses are built on piles above the ground, this being the easiest method of obtaining a flat floor, which can be kept dry in the rains on the sloping sites, whilst the space underneath forms a convenient stable or pigsty. Bamboo mats are used to make the walls of the houses, the thick grass thatch is extended to form wide pro-

<sup>4</sup> See B. Gupta, quoted by C. C. Lewis, I.C.S., in "A Note on the Palaungs of Hsipaw and Tawngpeng," *Ethnographical Survey of India, Burma*, No. 1, 1906, p. 3.

jecting eaves which keep the rain from the living rooms. There are open verandahs at one or both ends, and each house often shelters several families. The end timbers of the roof sometimes project in the shape of a V. The houses are placed anywhere and it is no uncommon occurrence for the floor of one to be on the same level as the roof of the next below. In the larger villages a more orderly arrangement is attempted and the houses line each side of a central road, furrowed like a ploughed field in the dry season and a bath of liquid mud in the rains, unless paved with stone. This central road extends as far as the two wooden uprights and cross piece, which denote the village gate, and are the only remaining symbol of the fortifications of earlier times.

### CUSTOMS.

The Palaungs possess all the fervour of the proselyte and Buddhistic ideas permeate some of their customs. Most villages have a "*pongyi kyaung*,"<sup>5</sup> and there the boys receive their early education in the law, much as young Shans or Burmans do. Courtship appears to be carried on, as it is with these latter peoples. Lowis has drawn attention to one habit which is unique and may be quoted:—"In some of the clans no youth is allowed to go a-courting until he has danced a *pas seul* at one of the principal festivals. Once he has 'come out' thus and acquitted himself creditably, the *débutant's* boyhood is looked upon as over and he is free to try conclusions with the maidens. Until this ceremony of initiation has been passed through, advances on the part of a would-be lover are always liable to bring on him rough treatment at the hands of the other bachelors of the community."<sup>6</sup>

Amongst many of the hill tribes of the Burma-China frontier there are customs which point to a time when marriage was entirely a matter of purchase. The Palaungs are no exception to this rule, but it is mainly in evidence now,

<sup>5</sup> Burmese = monastery.

<sup>6</sup> See Lowis, *loc. cit.*, p. 10. On this subject see also the following, *Upper Burma Gazetteer*, part 1, vol. i., page 489.



should the suitor be unfavourable to the girl's parents. The vast majority of the people live in a monogamous state. Polygamy only prevails amongst the wealthy and in the ruling family.<sup>7</sup> Endogamy does not exist; indeed, Palaung men often marry women of other tribes, but the easy sexual relations of some of these tribes are unknown. The young wife, as a rule, settles down with her husband in the home of his parents. As amongst the Shans, cremation is reserved for those of princely blood or of the priestly orders, the lay dead are buried.

### RELIGION.

On the surface the Palaung is an austere Buddhist of the strictest degree, in reality all the more important events of his life are ruled by animistic beliefs, and he pays scrupulous attention to the requirements of the *nats*—the spirits of the air, river, mountain, forest, house, and what not, good, bad and indifferent, as the case may be. These beliefs are certainly legacies handed down from his pre-Buddhist forefathers. Every village of any importance has its *pongyi-kyauing*, often a *zayat*<sup>8</sup> and sometimes a pagoda or two. Pagoda building is not carried on to so great an extent as it is in Burma, but this is only because the people are not so wealthy as the Burmese. Palaung women, who have become Buddhist nuns, are often seen. The tribe keeps the commandment, "Thou shalt take no life of any kind," so literally that it is sometimes difficult for the European traveller to obtain fowls for food. They make long journeys to visit famous shrines or to attend religious festivals, and I have myself seen them so far afield as at the Arakan pagoda in Mandalay and the Shwe Dagon pagoda, in Rangoon. Nevertheless, the superstitious practices of animism are carried on with punctilious care. *Nat* shrines and altars, where the spirits are propitiated, are common everywhere and have been seen close to the sanctified ground

<sup>7</sup> See *Burma, A Handbook of Practical Information*, p. 115, by Sir J. George Scott, K.C.I.E.

<sup>8</sup> Or rest-house.

around pagodas. An annual ceremony at which the *nats* are feasted is held every September in Namhsau by the Katurr clan of the Palaungs, who have a spiritual Sawbwa<sup>9</sup> as well as a temporal one.<sup>10</sup>

#### INDUSTRIES.

The Tawngpeng State is famous throughout Burma for the tea which it produces and the area is known to the Chinese as the "*cha shan*" or tea mountains. The article comes on the market as dried-tea or as "*let-ppet*," the moist pickled tea of the Burmese. Around the villages the slopes of the hills are usually covered with tea bushes, places being used which are so steep that one wonders how the soil is prevented from slipping off them. The jungle is cleared with the "*da*,"<sup>11</sup> but the position of the clearings necessitates the use of hand hoes. Very little trimming appears to be done to the bushes, and after the leaves are picked they are stored in pits, until they can be packed and sent down to Burma by railway or by bullock caravan. Small amounts of rice are grown, but the production does not suffice for the needs of the population, hence, it is a rule that caravans coming to the country for tea, must bring in rice as a condition of admission.<sup>12</sup> Palaung women always carry loads in a long basket on the back, supported by a strap across the forehead. Within recent years, extensive mining operations have been undertaken by European companies near the northern boundary of the State, but it is exceedingly doubtful if the Palaungs will be of any service, or will take to skilled labour of this kind.<sup>13</sup>

#### DRESS.

It is difficult to distinguish Palaung men from Shans, as the former copy the latter's dress, which consists of black, blue, or white, full, cotton trousers, a loose, blue, long-

<sup>9</sup> Or chief.

<sup>10</sup> This ceremony is described in the *Upper Burma Gazetteer*, part 1, vol. i., p. 491, and is referred to by Lewis, *loc. cit.*, pp. 22-23.

<sup>11</sup> A long-bladed heavy knife. <sup>12</sup> See Sir J. George Scott, *loc. cit.*, p. 483.

<sup>13</sup> See T. D. La Touche and J. Goggin Brown, *loc. cit.*

sleeved jacket, a blue or white turban, and a huge, soft, sun hat. The women, however, always wear a characteristic national costume, which varies from place to place, amongst different clans, but is rigidly adhered to in the minutest details. The following description of a Katurr woman's dress is taken from Lowis's note:—<sup>14</sup>

"The Katurr woman's full dress costume is both highly coloured and elaborate, and comprises a skirt (*glang*) of crimson cloth, crossed horizontally with thin—at a distance practically invisible—stripes of black, yellow, green and white, which reaches to the ankles, a short sleeved jacket (*kapran*) or smock, not unlike the '*thindaing*' of the Karen country, reaching to the waist with a V-shaped opening for the insertion of the head, and a large hood (*rangwi*) brought to a point at the back of the head and covering the greater part of the back of the body and legs. The smock is usually of cloth or velveteen, sometimes black, sometimes of some other colour that sets off scarlet well. The sleeves reach to the elbow and are of scarlet cloth and the neck opening is edged with cloth of the same colour. The front of the smock is decorated with a pattern of zig-zag stitching about six inches broad, below which comes a horizontal strip of scarlet cloth about two inches in depth and rather over a foot across. The hood consists largely of rectangular panels of scarlet cloth of different sizes sewn on to a foundation of coarse unbleached calico. The space immediately covering the back of the head is filled by an oblong patch of bright coloured damask plush, about eighteen inches by twelve and there are one or two smaller panels further down the back of the hood. Over the top front of the hood runs a two-inch wide strip of plush or velveteen, ordinarily blue or violet, which has a zig-zag pattern similar to that which covers the front of the smock, stitched or embroidered on it. The rest of the outer edge of the hood consists of a border, about six inches broad, of figured silk, velveteen or satin, designed like a good deal of the rest of the garment, to set off the scarlet of the panels. Over the skirt are worn three rect-

<sup>14</sup> See Lowis, *loc. cit.*, pp. 24 and 25.

angular apron-like pieces of scarlet cloth (*ratoī*) divided, like the hood, into oblong panels, with a patchwork border of cloth, ordinarily orange and green, and decorated with scarlet and orange tassels. These aprons are tied on round the waist behind and before and cover the skirt to within about a foot of its lower end. Leggings (*karjōng*), often of plush or velveteen, are worn under the skirt, and, in full dress, sleeves of silk or satin are slipped on over the wrists to meet the short sleeves of the smock and so cover the arm completely." Silver bangles, crescent-shaped silver torques and on special occasions silver waist-chains, are worn. "On gala-days gold studs (*hiaw krir*) are worn in the ears of the well-to-do and occasionally the back of the hood is decorated by a circular piece of embossed silver, known as a 'tum,' something like a dessert plate in size and shape." A tight fitting cap of black cloth decorated with silver wires is worn beneath the hood, but occasionally, as I have observed amongst the Katurr women at Saram, the hair, after being carefully combed, is allowed to hang over the shoulders. The skirt and groundwork of the costume is made of indigenous cloth, but the ornamented portions are purchased from Burmese and Chinese hawkers who sell imported materials.

Many of the women of the other clans wear costumes which are quite as complex as the one described above, so that the expert alone can tell at a glance to which clan they belong.

Mention must be made of the black-varnished bamboo hoops worn around the waist by some Palaung women, a custom also in vogue amongst the Chingpaw.

The highly elaborated dresses are usually worn on festive days, and the ordinary dress is a dark blue short jacket and a skirt and leggings. The curious emblematic design of the "svastika" is unknown to the Palaungs, though both Shans and Chingpaw use it largely.

The Palaungs of Namhsan claim to be descended from a "nagā" (dragon or serpent),<sup>15</sup> a claim often found amongst

<sup>15</sup> See *Upper Burma Gazetteer*, 1900, part 1, vol. i.; pp. 484-485.

the traditional records of Mon-Hkmer tribes and Lewis has suggested that a great deal of the seemingly meaningless decorative detail of the Palaung women's dress must at one time have been replete with symbolism—"The stripes and patches on the Palaung women's attire, the rings they coil round their necks, their foreheads, their waists and their legs, the diamond-shaped plates of silver that decorate the fronts of their jackets, may at one time have had some kind of connection with the bands and scales on the serpent's body and that the '*angwi*,' the most distinctive feature of their costume, may be identified with the hood that characterised the most fearsome of the reptiles that in the dim past the serpent-worshippers adored."<sup>16</sup>

There is certainly evidence which points to the prevalence of ophiolatrous practices amongst some of the Mon-Hkmer tribes in the remote past, though whether the tradition and dress referred to here are sufficient to include the Palaungs amongst them, the reader may be best left to judge for himself.

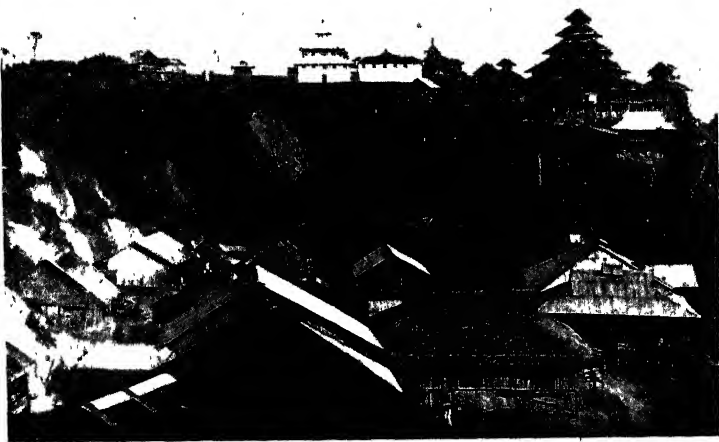
#### TRIBAL DIVISIONS.

The Palaungs have been divided by some writers into Palaungs proper and Palès, but although the division is convenient, it is foreign, being of Burmese origin, and is therefore not to be too closely relied on in any scientific classification of the tribe.

Lewis has enumerated some fourteen different clans from Tawngpeng and Hsipaw.<sup>17</sup> Some of these are well to do, others are backward and poor, some inhabit compact areas, whilst others are scattered. They are distinguished chiefly by variations in the colour, design and shape of the women's dress, and by slight dialectal differences. Until exact anthropometric data are available, it is impossible to say how far these are strict ethnical divisions, as distinguished from the outcome of the customs of a time when, for some reason or other, the Palaungs were split up into distinct endogamous communities.

<sup>16</sup> Lewis, *loc. cit.*, pp. 16, 17.

<sup>17</sup> Lewis, *loc. cit.*, p. 20.



*Photo by J. Coggin Brown.*

NAMHSAN, THE CAPITAL OF THE PALAUNG STATE OF TAWNGPENG, SHOWING THE CHIEF'S PALACE (THE WHITE BUILDING IN THE CENTRE OF THE PICTURE), AND A MONASTERY (TO THE LEFT).



*Photo by J. Coggin Brown.*



## ST. OSWIN AND TYNEMOUTH PRIORY.

By H. H. E. CRASTER, M.A., Fellow of All Souls, Oxford.

[Read February 24th, 1910.]

Eight hundred years ago this summer, on August 21st, 1110, there took place a ceremony important for its consequences in the history of the Northern Church—the consecration of the newly erected church of Tynemouth Priory, and the installation in the edifice of the supposed remains of St. Oswin.

Oswin was son of Osric, King of Deira. He spent his boyhood in exile, but at length succeeded in wresting his native county from the Bernician king, Oswy, and ruled it for seven years. At length, in 651, Oswy invaded Deira with the object of regaining the kingdom. Oswin collected his forces to oppose the Bernicians near Catterick, but found his army outnumbered and ordered a retreat, in the course of which he was betrayed to his rival and put to death.

His fame rests on the story of his friendship with St. Aidan. He had presented that bishop with a horse from the royal stables, and had learned with some annoyance that Aidan had given it away, royal caparisons and all, to a casual beggar. On their next meeting he reproached Aidan with his excessive charity. "Have we not," he said, "commoner horses and other breeds good enough for beggars? Why give away the horse which I picked out specially for you?" To this the bishop replied, "What, my lord? Is a mare's son dearer to you than Mary's Son?" It was the dinner hour, and the king went into the hall and stood among his thegns in front of the fire to warm himself. When the bishop came not, Oswin suddenly recollected his answer and apparent displeasure, and ran out and threw himself at the bishop's feet, asking forgiveness. Aidan, much troubled, raised the kneeling monarch and sat down with him at the banquet. So they all grew merry again, but Aidan became sad and let fall a tear. His priest



asked him, in the Celtic tongue (which Oswin and his company understood not), why he wept. "I know," he said, "that the king will die, for never e'er now have I seen a humble king."

To-day Aidan is commemorated, and justly commemorated, as one of the great leaders of the Northern Church, and Oswin's fame is almost forgotten. In the twelfth century it was otherwise. "I have long known of St. Oswin the king," said a citizen of Norwich (a widely-travelled man who had been thrice to Jerusalem), "but this is the first time that I have heard the name of St. Aidan the bishop."

And now we will leap four centuries, and come to the year 1065, and to a night late in February or early in March, in which we are told that Edmund, custodian of the little church of St. Mary of Tynemouth, had a dream. In his sleep a man appeared to him, and said, "I am King Oswin, who lie in this church unknown to all. Rise, go, and tell Bishop Egelwin that he seek my body in the floor of the chapel, and that, when he has found it, he raise it and place it in a more fitting place." Edmund did as he was commanded. He informed Egelwin, then bishop of Durham, of his dream, and on March 11th the bishop and many more came to Tynemouth and commenced their search for the saint. From morn to noon they dug without success; and most of the company whom curiosity had drawn thither, had tired of the hunt and dispersed. At last Edmund seized a spade, and, as he dug deeper into a part of the church floor which had already been trenched without success, the sharp ring of iron on stone heartened him to redoubled efforts. A stone coffin was bared and acclaimed as Oswin's. The human remains within it were reverently lifted out and replaced in a shrine supported on pillars in a raised portion of the church.

The reign of Edward the Confessor marked a religious revival which had for its outward sign the cult of the early leaders of the English Church and an ardent desire to obtain some tangible memorial of them. Ælfred Westou,

who was then sacristan at Durham, won especial fame as a relic hunter. It was his practice to visit the sites of the ancient monasteries and churches of Northumbria, to disinter the bones of the saints who were buried there, and to place them in shrines above ground for popular veneration. Amongst his discoveries are to be rehearsed the bones of St. Boisil at Melrose, those of the Venerable Bede at Jarrow, the remains of the hermits Balther and Bilfrid, of Acca and Alchmund, bishops of Hexham, of the abbesses Ebba and Ethelgitha, and, according to the Durham Chronicler, the body of St. Oswin. This version of the story (which is earlier in point of date than the other) places the discovery of St. Oswin's remains in its proper historical setting, as an incident in the general religious and national revival which marked the half-century before the Norman Conquest, as—if one may say so—a measure of church policy.

Although Tynemouth was a place of undisputed sanctity and the site of an important monastery in the days of the early church, no known historical authority had, previous to 1065, connected with it the name of St. Oswin. The saint met his death at Ingetlingum, a place usually identified with Gilling, near Richmond. There, in all probability he was buried, and there Oswy's mother, Queen Æanfled, built a monastery where prayers were unceasingly made for the two kings, Oswy and Oswin, the slayer and the slain. Can there have been confusion on the part of the finder, wittingly or unwittingly, with Osred, also a Northumbrian king, also one who lost throne and life at the hands of a rival, and who undoubtedly was buried (A.D. 792) at Tynemouth?

In 1074, nine years after the discovery of St. Oswin's body, Waltheof, Earl of Northumberland, gave to the monks whom Bishop Walcher had lately settled at Jarrow, the church of Tynemouth, and, with it, the body of St. Oswin. The monks celebrated mass regularly in the church, and from time to time ferried the saint's body across the Tyne

to Jarrow, afterwards replacing it at Tynemouth when the brethren had no longer need of their sacred treasure. When the Jarrow monks were transferred to Durham in 1083, one of their number, named Turchil, was sent to reside at Tynemouth, but in 1085-6, or possibly as late as 1090, upon the occasion of a quarrel between Carileph, Bishop of Durham, and Robert Mowbray, Earl of Northumberland, the earl evicted the monk Turchil from Tynemouth, and conveyed the church, which he had thus appropriated, to the Abbot of St. Alban's.

By this chain of events Tynemouth passed away from Durham to St. Alban's, and, from being a parish church, placed under the care of a solitary monk, became a self-contained monastery, inhabited by a religious community. The change necessitated the erection of conventual buildings and the construction of a new church adapted to the use of a resident body of monks as well as of the pilgrims who came to worship at the shrine of St. Oswin. In 1093, Paul, Abbot of St. Alban's, came to inspect his new cell. His visit may mark the commencement of the Norman monastic church, which we knew to have been completed in the year 1110. On August 21st of that year, being the anniversary of St. Oswin's passion, the shrine of St. Oswin was removed from the little pre-Conquest church in which it had hitherto rested, and was placed in the new edifice in the presence of the bishop of Durham, the abbots of St. Alban's and Selby, and a great gathering of clergy and laity.

In 1176, a long lawsuit, which had been carried up to the papal court, was terminated by the prior and convent of Durham, relinquishing their claims to Tynemouth in return for a grant of two parish churches which had formed part of the endowment of Tynemouth Priory. Having thus bought off Durham Priory, the monks of Tynemouth found themselves in a better position to assert their independence of the distant abbey of St. Alban's. With the sanction of Henry II., they elected Akarius, one of their own number, to be prior. Akarius was forthwith

admitted and instituted without reference to the abbot of St. Alban's. It is to his priorate that we must assign the extension of the monastic church, and the erection of that great eastern arm, containing choir and sanctuary, which forms the most striking and impressive portion of the existing ruins, and in which we may possibly see a projected northern abbey, rivalling Durham and free from St. Alban's.

The demolition of the Norman choir and the extension of the church eastwards probably necessitated the removal of the high altar, and, with it, of St. Oswin's shrine. A goldsmith, named Baldwin, was employed by Prior Akarius to decorate the shrine with gold and silver. He was celebrated for his skill in metal-work, particularly in floral ornament, and had been employed by Simon, Abbot of St. Alban's, a great patron of art, for whose monastery he made, amongst other things, a gold cup, described by Matthew Paris, half a century later, as the finest that he had seen in England. His name occurs in the Northumbrian Pipe Roll for 1186 as plaintiff in an action for debt; and, as we are expressly told that he made no long stay in the service of the prior of Tynemouth, the entry approximately dates the time when he was working upon the shrine.

Once again, in the fourteenth century, the body of St. Oswin was moved. Of none of the priors of Tynemouth have we a more complete portrait than of Thomas de la Mare, who ruled in Tynemouth as prior from 1340 to 1349, and was afterwards for forty-seven years abbot of St. Alban's. The splendid Flemish brass which covered his tomb still exists at St. Alban's and preserves his features. Scholarly, courteous, charitable, he made himself loved by all who met him, from the Black Prince (who was his especial friend) down to the sick and the lepers whom he personally tended. He had a natural dignity, a ready wit, and a practical mind. So that it is not surprising to find Edward III. saying of him in later days:—"In person, breeding, and humanity, there is no abbot in my kingdom who can compare with him."

During his tenure of the office of prior at Tynemouth, he spent much money upon buildings. Amongst other changes introduced by him into the disposition of the church, he removed the shrine of St. Oswin from the high altar to a part of the church where it might be more conveniently visited by pilgrims without interrupting the monks at their services. Possibly its new home was the Lady Chapel which had been erected, some fifteen years earlier, at the north-east angle of the church. Before the close of the same century Joan, Princess of Wales, widow of the Black Prince, gave a donation for the adornment of St. Oswin's shrine.

At that shrine Edward I. had knelt and made oblations. It no longer worked miracles, or the miracles have been unrecorded, but its fame lasted on to the suppression of the monasteries. Of its demolition we have no direct record, and the last scene would have been lost to us were it not that a certain Christopher Chaytor, servant to Tunstall, Bishop of Durham, had told of how, one Sunday, travelling along the London road from Huntingdon, he overtook two men and rode past them. But one of them, named Cray, followed, and asked what news and why he rode so fast; and, so falling into conversation, enquired whether there were any abbeys in the North still standing. Chaytor answered, "They shall down shortly, by report." Then he asked, "How doth your shrines? Are they taken away?" And Chaytor said that there was one at Tynemouth, where he had seen the King's commissioners handling the relics very irreverently, despoiling them of their gold and silver, and casting them away. They gave him some bones garnished with silver; "and he that gave me them," said Chaytor, "said the silver thereof would make a chape to my dagger." He said he had them still, and would have great need ere he should sell them; "for, as I have heard a learned man say (which was Dr. Ridley that is dead), St. Jerome and St. Ambrose held these relics of saints in honour."



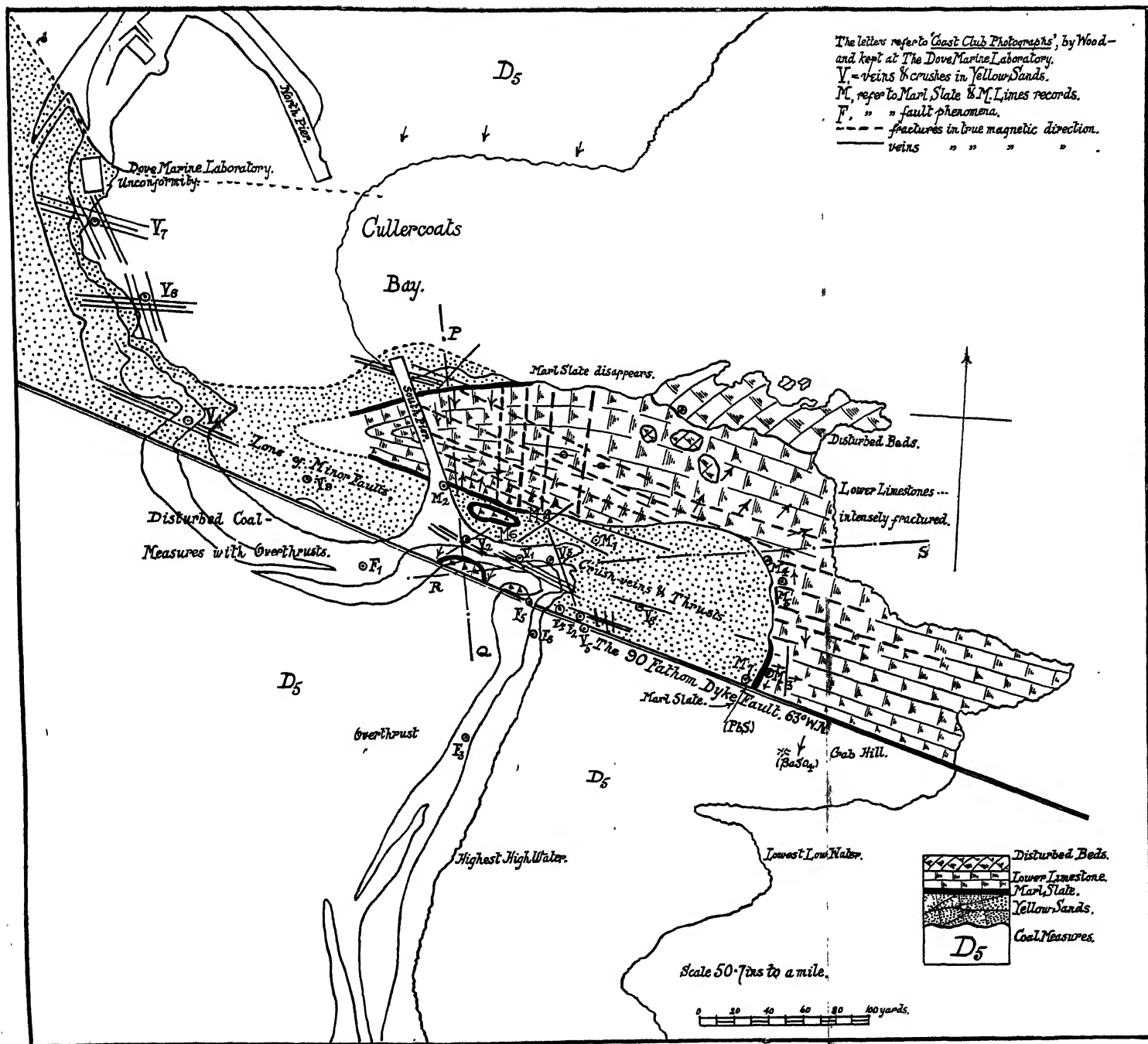


FIG. 1.







## SOME PHENOMENA IN THE PERMIAN OF NORTHUMBER- LAND AND THEIR RELATIONSHIP TO SECTIONS IN DURIAM AND CUMBERLAND.

By S. RENNIE HASELHURST, M.Sc., F.G.S.

[Read December 6th, 1910.]

It is the object of this paper to describe some unrecorded features of the Permian of Northumberland and to offer an explanation of the origin of these. The work was undertaken after reading Lebour's paper on the Marl Slate and Yellow Sands<sup>1</sup> and through the inability to reconcile certain facts shown on Geological Map (Sheet 89; 6 inches to a mile) with actual observations. New exposures of the Marl Slate in the Cullercoats area led to the re-mapping of the district. This was done on a scale of 50·7 inches to a mile and the results are shown in Fig. 1.

### THE CULLERCOATS AREA.

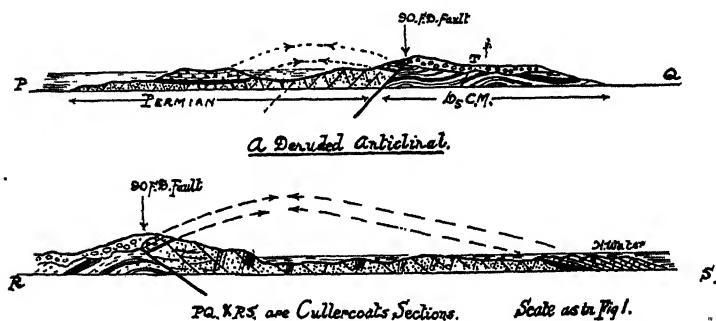
The Cullercoats area of Fig. 1 may be taken as strictly typical of the Lower Permian divisions. In the Geological Survey (Sheet 89, 6 inches to a mile) the D<sub>s</sub> Coal-measures and the Permian are shown as being faulted by two normal, *proved* faults, the Ninety Fathom Dyke fault and a parallel fault having a mean trend of N. 76° to 82° W. The Yellow Sands are thus made to abut upon the Ninety Fathom Dyke Fault. The series is again faulted to the north of this by a proved normal fault hading at a high angle to the N.W. and having a throw of about 10 feet.

A careful examination of the area between the Ninety Fathom Dyke and the latter fault showed four exposures of the Marl Slate lying conformably upon the Yellow Sands. These are seen in Fig. 1, at R, M<sub>6</sub>, M<sub>3</sub>, M<sub>7</sub>. At R the Marl

<sup>1</sup> *Trans. Inst. of Min. Eng.*, 1902-3, vol. xxiv., pp. 370-391.

Slate and Lower Limestone dip in to the fault, at  $M_6$  they are horizontal, at  $M_2$  away from the fault and at  $M_3$  to the east.

It appears, therefore, that the area is a denuded dome, and sections over it would therefore be as in Figs. 2 and 3. But on tracing the Marl Slate from  $M_2$  to  $M_4$ , to  $M_3$  and  $M_7$  it first disappears and then re-appears. It should be noticed that east of  $M_7$ ,  $M_3$ , the Marl Slate and Magnesian Limestone abut on the fault and *not* the Yellow Sands, as some writers have made it.<sup>2</sup> This discrepancy was noted by Hutton in 1830.<sup>3</sup> To explain the disappearance of the



FIGS. 2 AND 3.

Marl Slate a short description of the other members of the series is given. At Cullercoats Bay the section is:—

						Feet.
Bedded Limestones (disturbed)*	...	...	...	...	...	6 (?)
Thrust Plane*	...	...	...	...	...	—
Bedded Limestone	..	...	...	...	...	6
Marl Slate	..	...	...	...	...	3
Yellow Sands	...	...	...	...	...	70 (?)

\* These correspond in position with their occurrence in Frenchman's Bay, south of the Tyne, where they have been described by Woolacott. *Univ. of Durham Phil. Soc. Mem.*, No. 1, 1909.

The Bedded Limestones are similar to those of Tynemouth and elsewhere, and it is but necessary to add that the upper beds are here, as at Tynemouth, thrust over the

<sup>2</sup> Sedgwick, *Geol. Trans.*, second series, vol. iii., plate iv., fig. 2.

<sup>3</sup> Hutton, *Trans. Nat. Hist. Soc. Northd. and Durham*, vol. i., p. 72.

lower beds with brecciation, so well shown in the Marden Quarry Section where the series runs:—

	Feet.
Brecciated Limestone*	20
Thrust Plane* ... ..	— (?)
Disturbed Beds* and Bedded Limestone ... ..	20
Marl Slate ... .. 3 ft. 6 in. <sup>4</sup>	} These are not now visible.
Yellow Sands ... .. (?)	

\* These correspond in position with their occurrence in Frenchman's Bay, south of the Tyne, where they have been described by Woolacott. *Univ. of Durham Phil. Soc. Mem.*, No. 1, 1900.

In the Bay the Lower Bedded Limestone is severed by a series of fractures parallel to the axis of the dome (Fig. 1) and in direct geometrical relationship to a *regular* series of veins in the Yellow Sands underlying it (Figs. 4, 5, 6). That great pressure and crushing has taken place is evidenced by the formation of new structures and minerals along these planes the rock being converted into a hard, grey, indurated limestone greatly resembling the Mountain Limestone and very highly calcareous. The Marl Slate is caught up at  $M_s$  and jammed against the Yellow Sands. Everywhere, upon examination along the outcrop, it is beautifully slickensided horizontally along the laminae, and these slickensides—which are characteristic of the Marl Slate whenever it has been thrust and sheared—pass into small puckers and folds, with the result that good fossils are very hard to get. Through the kind courtesy of Dr. A. Smith Woodward, F.R.S., I have been able to recognise teeth of *Acrolepis* and *Pygopterus*, scales of *Palæoniscus* and *Cœlacanthus*.

*The Yellow Sands.*—At Cullercoats this deposit attains a minimum thickness of 70 feet (?). No definite horizons have up to the present been determined. In the outcrop it is noticed to be traversed by a series of hard calcareous ridges shown in Figs. 4, 5. These are quite regular, as a careful analysis of their magnetic bearing will reveal. From numerous observations they have been classified into two series, those running parallel to the Ninety Fathom Dyke fault and those bearing counter to it. The average bearings are:—

<sup>4</sup> Lebour, *op. jam cit.*, p. 15.

(a) N. 42° W.

(b) N. 99° W.

Thus the (a) series are practically normal to the N.E. bearing fault, hading to the N.W., and the (b) series differ but slightly from the trend of the Ninety Fathom Dyke. In section these veins appear as small faults of definite hade to the north; they are multitudinous in number and are termed "minor faults." In Figs. 4, 5 they are seen to be counter to the "crush veins," which pass through them in some cases and are subsequent in formation to them. These

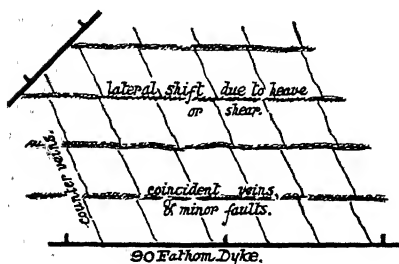


FIG. 4.

crush veins dip in to the Ninety Fathom Dyke fault at a somewhat sharp angle. It is to them that we must look for evidence of lateral heave or displacement. This is important, for it is found to be everywhere characteristic of this type of deposit when it has been

subjected to shears and strains. These planes show distinct displacement and definite shearing eastwards and the mass of sand is divided into lozenges laterally displaced (Fig. 4). This proves a shear from the west. The minor faults afford planes of varying hade along which the whole formation to the north has been sheared and thrust. This thrust would take place naturally along lines of least resistance and the beds of more rigidity would move over the Marl Slate or along the horizontal bedding planes of the Magnesian Limestone. Thus the Marl Slate would become obscured along the plane perpendicular to the thrust by "squeezing out" and would be preserved as at M<sub>2,6</sub>, by tilting due to lateral pressure. Resistance to this thrust would fracture the dome and render it liable to easy denudation. Adopting the view taken of a lateral shear along the plane to the east and acting conjointly with the thrust from the north we can easily account for the anticlinal form at Cullercoats and the preservation

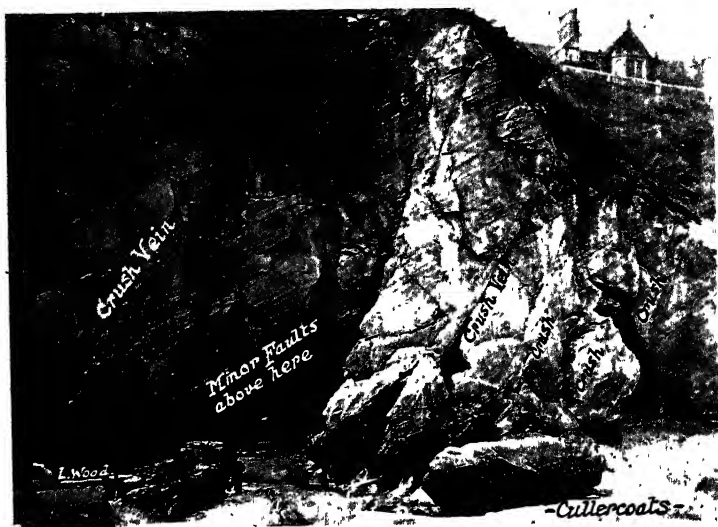


FIG.

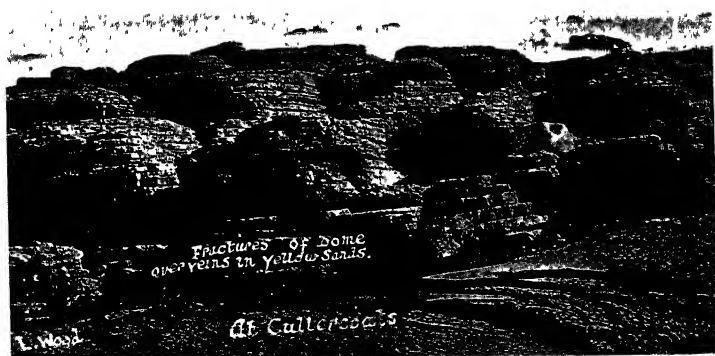


FIG. 6.



of the Marl Slate at M<sub>2</sub>. The disturbed beds are also easily accounted for and naturally as the low hade of the Ninety Fathom Dyke fault (38° N.) formed a buffer these limestones would fracture as shown in M<sub>4</sub>, M<sub>3</sub>, M<sub>5</sub>, and Fig. 6.

It would appear from the foregoing:—*That a thrust took place from the north perpendicular to the Ninety Fathom Dyke plane, the slipping face of the N.E. fault acted as a buttress, and by the pressure in its check caused a shear to the east, as is shown by the Yellow Sands.*

Hutton<sup>5</sup> writes with reference to Marden Quarry, Whitley:—

“ In the south side of the quarry, in several places where the limestone is worked near the line of the Dyke, marks of mechanical action were visible, particularly near the railway on the eastern side. The general opinion is that this patch of limestone overlies both of the edges of the Dyke and that it has been deposited, not only after the slip took place, but after the removal of the whole of the high side which would necessarily be left by the sinking down of the strata on the north. This is an opinion from which I confess I differ with reluctance. As the limestone is manifestly thrown down along with the Yellow Sands and *contorted by mechanical action*, we are compelled to come to the conclusion that the Ninety Fathom Dyke was formed after the deposition and consolidation of the Magnesian Limestone, and this would necessarily be our conclusion, if there *were* no marks in the quarry to point it out, as we cannot suppose the limestone in the two situations to be of different ages or, closely connected as they are, to be operated on by different causes. The idea of the limestone overlying the dyke may possibly have arisen from it being considered a perpendicular fissure, which it certainly is *not*, either in the quarry at Whitley or at Cullercoats or at Gosforth.”

<sup>5</sup> Hutton, *op. jam cit.*



This is quoted *in extenso*, because of its very great significance in this connection. It manifestly indicates a difficulty which, on the acceptance of the proof of a thrust from the north, entirely disappears. A huge mass of Limestone is here clearly mechanically disturbed and overlying both cheeks of the Ninety Fathom Dyke fault which he clearly stipulates is *not* a vertical fissure but a fracture of very low hade, *i.e.*, one which I have shown to be a plane along which actual thrusting took place—the plane of the “minor faults” and “crush veins.” Further evidence being necessary, we need but to look at the recorded position of the major thrust plane proved by Woolacott in both of the Cullercoats sections (page 16). This section has also clearly shown the *nature of a thrust acting on the less resistant members of the Permian in this area.*

#### THE TYNEMOUTH SECTION.

The sequence at Tynemouth is—

SECTION A, FACING E.	SECTION B-C, FACING N.E.
South end of Section.	North end of Section.
1. Brecciated Cellular Limestone ... .. 18'-20'	1. Brecciated Cellular Limestone ... .. 10'-15'
2. Thrust plane.	2. Thrust plane.
3. Bedded Lower Limestone, with ferruginous nodules. 5' A sandy and concretionary limestone with geodes pseudomorphous after pebbles, encrinite stems 6'	3. A series of alternations of marls (yellow, greenish and black), limestones and sandstones, very regular stratified and little disturbed ... .. 18'
4. Marl Slate with <i>Acrolepis</i> scales ... .. 3'	4. Marl Slate with <i>Paleoniscus</i> ... .. 3'
Yellow clay puckered and slickensided ... .. 3"	
Red sands ... .. 3"	
Yellow Sands, with crush veins, minor faults, and	5. Yellow Sands ... .. 1'
5. false bedding ... .. 20'-22'	Magnesian Limestone ... .. 6"
Unconformity.	Yellow Sands ... .. 1' 6"
Coal measures.	Yellow and Red Marl ... .. 1'
	6. Unconformity.
	7. Coal Measures.

This sequence is of interest for two reasons:—First, the Marl Slate is for the first time placed in its true relationship

to the Yellow Sands, lying conformable to it.<sup>6, 7</sup> Its fossils have been identified as at Cullercoats (*Aerolepis*, *Palæoniscus*). Secondly, it shows the disturbed beds of Woolacott in the Upper Bedded Limestone, the thrust plane and a mass of Brecciated Limestone capping the cliff as on the south of the Tyne. It clearly indicates the thrust effect upon the Yellow Sands by the development of fractures and minor faults in it and the superincumbent limestone. [It is interesting to note that Hutton records several faults traversing the whole formation in the eastern face.<sup>8</sup>] The section provides one more feature of considerable interest, in a mass of Limestone so highly siliceous as to be almost a sandstone. It is about a yard thick and lies above the Marl Slate and conformable with it. In its upper layers, whilst massive, it presents crude beds consisting of what appears to be "dedolomitized" pebbles with a geode interior of "dog-tooth spar."

It appears from the foregoing that the major thrust plane of Durham extends northwards as far as the Ninety Fathom Dyke as an unbroken record of similar phenomena impressed upon the whole formation. From the foregoing work on the Yellow Sands the following hypothesis was put forward with reference *only* to a sandy formation:—

- (a) If a series be faulted by a major fault so as to bring on the downthrow side a friable sandy formation against a fault plane, then the sandy formation will show the development of minor faults accompanied by shears, crush veins, and thrusts. Or, conversely,
- (b) If crush veins, minor faults and shear planes occur in a sandy formation, they indicate by their magnitude, direction and hade those of the major fault, even if it be obscured.

<sup>6</sup> Sedgwick, *op. jam cit.*, Pl. vi., Fig. 1.

<sup>7</sup> Lebour, *Geology North. and Durham*, p. 35 and section.

<sup>8</sup> Hutton, *op. jam cit.*, p. 65.

This hypothesis was independently tested at Seaton Sluice, Claxbeugh, and at many parts of the Eden Valley. In each case visited it was known that there were two common factors, the fault and the sands. Veins and minor faults and lateral shears established in the typical area by pure deduction were found to exist in every section examined, however remote. In 1909, the Eden Valley sands of Permian age were investigated in the same manner. Here

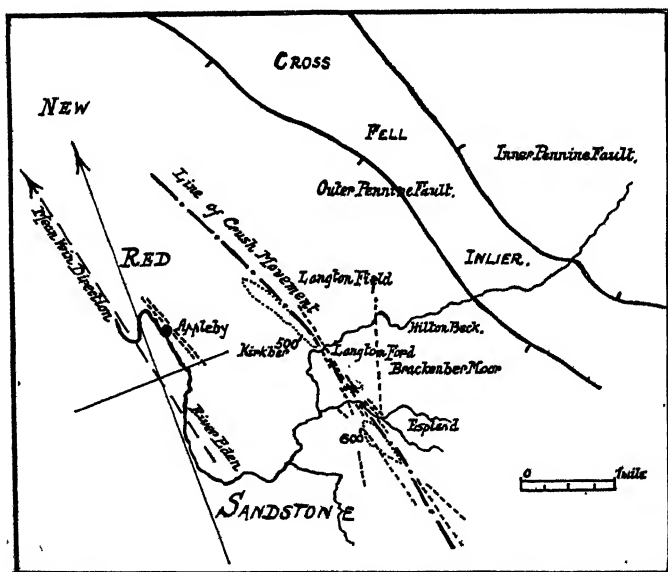


FIG. 7.

the New Red Sandstone and Hilton Plant Bed, the equivalents of those examined in Northumberland, are brought down to the west by the major Outer Pennine Fault (Fig. 7), which fades to the west. A type section was worked out in Easter, 1909, in Hilton and Murton Becks, and since then the writer has visited every important exposure from the Nunnery at Kirkoswald, southwards and finds that phenomena answer to the prediction. The sandstone for a definite zone parallel to the Outer Pennine Fault

is reticulated with extremely hard siliceous vein masses (coincident veins) parallel to the fault. These may be illustrated by inverting Fig. 4. They show marks of great shearing and thrusting, being most beautifully slickensided, even grains of sand being "dragged out." Two types of veins intersect, as at Cullercoats, their bearings being—

(a) N.  $60^{\circ}$  E.

(b) N.  $11.5^{\circ}$  W. (parallel to O.P.F.).

Whilst not proved, it seems possible that the (a) series are related to the transversal faults of the Cross Fell inlier. Thrusting appears to have taken place from the west (the Horst of the Lake District) and shearing northwards, parallel to the Outer Pennine Fault. The plane of movement appears to be that shown in Fig. 11. It was a pleasure to find two months later that Professor Percy Kendall<sup>9</sup> had established movement along the Outer Pennine Fault Plane to the extent of 1,000 feet in post Permian (?) times. This was proved entirely on different lines from a petrological knowledge of the Brockrams.

In conclusion, I wish to thank Dr. Woolacott most heartily for kindly visiting the Northumbrian sections with me; Mr. Lionel Wood for his excellent photographs, which helped to unravel many a puzzle; and Miss Heslop and Mr. George Duncan for their kind assistance with lantern slides and microphotographs.

NOTE.—All maps, photographs, lantern slides and models illustrating this paper can be seen on application to Professor Meek at the Dove Marine Laboratory, Cullercoats.

<sup>9</sup> Kendall, British Assoc., Report of Meeting, 1902, p. 604.

## ON THE FORMATION OF KAOLINITE IN SOME COAL-MEASURE SHALES.

By R. COOKSEY BURTON, B.Sc.

[Read December 13th, 1910.]

It has long been known that shales are, for the most part, mixtures of hydrated aluminium silicates, among which kaolinite has been supposed to occur; it is my object, in this paper, to show how pure kaolinite has been formed by the alteration of certain clay-ironstones and coal-measure shales and has recrystallised as a white mineral almost chemically pure.

The localities at which I have observed kaolinite under these circumstances are as follows:—

- (1) In the Mussel-Band at Whitley Bay above the Low Main Coal.
- (2) In the Mussel-Band at West Wylam Pit above the Beaumont Seam (?)
- (3) In a shale from the Duke Pit, Ashington.

The conditions under which the beds containing kaolinite occur are different in each case, so that it is necessary to append a short description of each.

(1) The Mussel-Band at Whitley Bay crops out on the sands below the Convalescent Home and below the promenade; the strike, as a general rule, being N.N.W. It is a clay-ironstone of a brownish black colour, turning reddish to a slight extent on weathering owing to the production of ferric oxide from ferrous carbonate, which is the main constituent of the bed. It contains small white patches of kaolinite, where the reactions described below have taken place. An important point to notice is that the kaolinite has been produced in the Mussel-Band at its actual outcrop.

(2) The specimens containing kaolinite at West Wylam

were collected from a heap of shale and other material which, having a fresh appearance, had evidently been brought to ground only a short while before. In this pit an anthracosia band occurs just above the Beaumont Seam and is assumed to be the source of the above-mentioned specimens. The bed is, in appearance, much the same as that occurring above the Low Main Seam at Whitley Bay, and its composition is probably very similar. It is worthy of remark that the kaolinite in this instance occurs at a considerable depth from the surface and consequently the conditions favouring its production are not quite the same as at Whitley. It seems probable also, from a consideration of these facts, that kaolinite, although occurring in very small quantities, is fairly generally distributed throughout the Mussel-Bands. It may be remarked, however, that it has been looked for in other places, particularly in Low Prudhoe Pit, without success.

The Mussel-Bands, as their name implies, are crowded with specimens of a fresh-water or estuarine mollusc, *Carbonicola aquilina*, which testify to the conditions under which the beds were deposited; their exact mode of formation is a question which we hope to discuss at some future date. The fossils are invariably distorted, sometimes only slightly; they are composed of calcium carbonate, which is comparatively hard and brittle, while the bed in which they lie is of a yielding nature. The probable cause of the distortion of the fossils is thus connected with their excessive crowding in soft shaly material upon which considerable pressure has been brought to bear.

In the Mussel-Bands, as they ordinarily occur, the individual shells are composed of calcium carbonate, while their interiors are filled with clay-ironstone or with secondary calcite which is optically discontinuous with the shell material. But when the bed has weathered under the conditions suitable for the production of kaolinite, the shell material has disappeared either wholly or in part, generally the latter, and has been replaced by kaolinite, while the

interior is unaltered; what remains is thus practically a shell of kaolinite, or composed partly of this mineral and partly of calcium carbonate. The replacement is thus seen to be a gradual process and it is probable that when kaolinite has taken the place of a portion of the shell, the actions described below are greatly retarded, so that further replacement is impeded owing to the screening of the remaining shell material from the air; this is discussed in detail below. Before proceeding to the treatment of the subject from the chemical side, it will be as well to complete the descriptions of the manner of occurrence of the kaolinite.

At Ashington kaolinite was found in the Duke Pit coating one side of a fine-grained, unfossiliferous shale, which is traversed by fissures. The strata are much disturbed, being faulted by the "Forty Fathom Trouble"—one of the numerous East and West faults crossing the Northumbrian coal-field. The kaolinite is fairly plentiful and covers that side of the shale which forms the wall of the fissures. The movement in the beds has been considerable and the rock is beautifully slickensided.

The conditions surrounding the formation of the kaolinite are clearly different from those affecting the Mussel-Bands. The kaolinite was proved to be such by microscopical and chemical tests, so that no doubt exists as to its purity. Its specific gravity is 2.58 and under the microscope it is seen to consist of silvery white flakes, which are colourless when mounted in balsam, with a perfect basal cleavage and giving a biaxial figure in convergent light; as is usually the case, hexagonal plates of the mineral are sparingly distributed. The specimen from Ashington was exceptionally pure. In the analyses given in Lebour and Smythe's paper on "An Unconformity and Thrust in the Coal-measures of Northumberland,"<sup>1</sup> the Mussel-Band is seen to contain a large percentage of ferrous carbonate, which weathers to ferric oxide and liberates carbon-dioxide. This dissolves in water already

<sup>1</sup> *Quart. Journ. Geol. Soc.*, 1906, p. 542.

containing the gas dissolved from the air and slightly strengthens the solution, which dissolves away the carbonate of the shells leaving hollow spaces subsequently filled, in some cases, by kaolinite. This action is, to a large extent, due to the atmospheric carbonic acid, but is no doubt aided by the gas liberated in the oxidation of ferrous carbonate. The Mussel-Band also contains about 10 per cent. of material insoluble in hydrochloric acid whose composition is seen in Analyses III. and IV.:—

	I.	II.	III.	IV. <sup>2</sup>	V.
	Kaolinite occurring in		Insoluble portion of Mussel-band.		Calculated for Kaolinite, $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$ .
	(a) Mussel-band, Whitley Bay	(b) Shale from Duke Pit, Ashington.	(a) Whitley Bay.	(b) Buddles' Hartley Colliery.	
H <sub>2</sub> O ... ..	16·83	13·93	22·56	18·75	13·90
SiO <sub>2</sub> ... ..	40·91	46·82	47·24	51·92	46·64
Al <sub>2</sub> O <sub>3</sub> ... ..	41·53	39·44	21·72	27·21	39·46
CaO ... ..	(Small amount).	—	0·08	1·65	—
MgO ... ..	Trace.	—	0·70	0·56	—
Na <sub>2</sub> O ... ..	Trace.	—	4·42	—	—
Fe <sub>2</sub> O <sub>3</sub> ... ..	—	—	3·39	—	—
	99·27	100·19	100·11	100·09	100·00

In III. and IV. the constituent quoted as water also contains organic matter. The agreement between the above two analyses is satisfactory, considering the fact that the percentage of organic matter is subject to variation according to locality and other circumstances.

It is obvious that there is a certain relation between the composition of the insoluble residue in the Mussel-Band and the kaolinite, which may be considered to have been formed from it in the following way:—

The soluble portion of the clay-ironstone is removed by the action of carbonic acid, produced partly in the weather-

<sup>2</sup> "Analyses of Rocks of the Coal Formation," by Hugh Taylor. *Trans. N. Engl. Inst. Min. Eng.*, vol. iii., 1854-5, p. 11.



ing of ferrous carbonate but mostly from the atmosphere, and this action most probably proceeds simultaneously with the removal of the shell material of the carbonicolas.

From the comparatively small percentage (c. 2 per cent.) of ferric oxide in the Mussel Bands it seems probable that the removal of iron as bicarbonate is more rapid than the oxidation of the normal carbonate to ferric oxide. The residue left is a mixture of hydrated silicates—some containing sodium and more unstable than the simple hydrated aluminium silicate.

By the continued action of carbonic acid, aided possibly by organic acids, this residue is decomposed, the more unstable silicates are removed, and it seems likely that a material resembling kaolinite in composition is left behind. This is recrystallised and part deposited in the spaces vacated by the shell material. That there has been a transference and recrystallisation of kaolinite is suggested by the fact that the material filling the interior of the shells is practically unaltered.

It is not to be supposed that all the kaolinite fills the spaces left by the dissolved shell material, since some occurs in places unconnected with these; but it is certainly curious that a kaolinite "shell," as described above, should be produced. The chief reagent in the above reactions is carbonic acid, which, in long-continued action, is known to exert a powerful decomposing effect on some of the silicates in rocks. At West Wylam, where the kaolinite occurs below the surface of the ground, percolating waters containing carbon dioxide in solution are probably responsible for most of the above changes.

It is interesting to note that kaolinite occurs sparingly in the pebbles of the conglomerate at and near the base of the Table Rocks Sandstone at Whitley Bay; this furnishes additional evidence proving that the pebbles were derived from the Mussel-Band.<sup>3</sup>

<sup>3</sup> Lebour and Smythe, *Q. J. G. S.*, 1906, p 542.

The occurrence of kaolinite in these small pebbles suggests that it was formed in the Mussel-Band before the period of unconformity; but upon this point it is best to be silent until something in the nature of proof is obtained.

We have to deal lastly with the kaolinite from Ashington. It has probably been produced by the action of carbonic acid on the mixture of silicates composing the shale. It is suggested that the more unstable were decomposed and carried away while the simple hydrated aluminium silicate, kaolinite ( $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$ ) was left behind and recrystallised. It is noteworthy that the mineral lines fissures down which water would have free play. Considerable heat would be generated in the movement of the beds and this may have aided in the reactions.

The above examples of the formation of kaolinite have been considered together as they all probably depend on the solvent action of carbonic acid. The occurrence of kaolinite in the anthracosia bands is a matter of interest, as part of the shell material of *carbonicola aquilina* has been replaced by this mineral.

In conclusion, I desire to acknowledge my indebtedness to Dr. Smythe for his helpful criticism and advice.

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## ON THE INTERACTION OF THE CONDENSER AND AIR-PUMP.

By JOHN MORROW, M.Sc., D.Eng.

[Read January 20th, 1911.]

The modern problem of obtaining the highest practicable vacuum in condensers associated with the steam turbine is complicated by several factors which had not previously become of great importance. In this problem two questions are especially prominent. The first concerns the rate at which heat can be transmitted from a flowing mixture of steam and air, through the walls of a metal tube, to the water which conveys the heat from the condenser. Although every experiment in which observations are made on a condenser deals more or less intimately with this subject, the final solution is scarcely within sight. The physical experiments of J. A. Smith constitute a valuable preliminary step.<sup>1</sup>

The second question concerns the interaction of the condenser and the air abstractor; it is to some extent amenable to theoretical analysis, and forms the subject of this paper. Professor Weighton's classical experiments on condensers<sup>2</sup> and a paper by Mr. D. B. Morison on the influence of air on vacuum<sup>3</sup> provide practical data and go far towards the elucidation of the subject.

When a mixture of steam and air is at rest in a non-conducting vessel the conditions accord with the law of Dalton and Gay Lussac. On the other hand, if the vessel be traversed by thin-walled metallic tubes kept at a low temperature by circulating water, the conditions are not those of thermal equilibrium. The relative quantities of air and vapour cannot then be determined by Dalton's Law.

<sup>1</sup> "Air in Relation to the Surface Condensation of Low Pressure Steam," by Jas. Alex. Smith, Victorian Inst. of Engineers, see *Engineering*, vol. 81, p. 395.

<sup>2</sup> "The Efficiency of Surface Condensers," by Prof. R. L. Weighton, Inst. Naval Architects, April, 1906; *Engineering*, April 13th and 20th, 1906.

<sup>3</sup> "The Influence of Air on Vacuum in Surface Condensers," by D. B. Morison, Inst. Naval Architects, April, 1908; *Engineering*, April 17th, 1908.

The modern surface condenser, however, differs from both the above cases in that it is specially constructed to give a general velocity to the air and vapour, from the exhaust branch at which it is admitted to the air pump suction, through which the air, and whatever vapour remains, is abstracted. Under these circumstances it appears likely that the constitution of the flowing mixture will be more or less closely in accordance with the law of partial pressures.

It is worth while, then, to trace out the physical changes which this mixture undergoes during its passage through the condenser.

To eliminate undesirable factors we may make certain assumptions which characterise what may be described as a theoretical or ideal condenser. They are as follows:—

- (1) That the water of condensation is drained away simultaneously with its formation;
- (2) That the pressure in the condenser is uniform throughout;
- (3) That the law of partial pressures is satisfied by the mixture of vapour and air whilst flowing through the condenser.

For an investigation dealing with the rate of heat transfer or of conduction through the walls of the tubes the above assumptions would introduce considerable errors; this paper, however, is concerned only with the varying temperature of the mixture and the corresponding changes in its volume and heat contents, and for these purposes the above assumptions are more or less justifiable.

The entry of air, in association with the steam, produces two important effects. The first is that condensation is retarded, and the second that condensation must necessarily be accompanied by a continuous decrease in the temperature of the fluid passing through the condenser.

This fall in temperature is the factor upon which the interaction of the air-pump and condenser depends; it is, of course, accompanied by a reduction of the pressure of the vapour and a corresponding increase in the partial pressure and

density of the air. The magnitude of the temperature fall is determined by the condenser and the resulting increased density of the air renders it more readily capable of abstraction by the pump.

The process can be best illustrated by a numerical example. Table I. refers to a condenser in which the absolute pressure is 1.005 pounds per square inch; the corresponding temperature would be 102° Fahr., but the presence of 0.0048 pound of air in each pound of exhaust steam, reduces the temperature of the mixture to 101.9° Fahr. The table shows the varying composition of the mixture during its progress through the condenser.

TABLE I.

Temperature of Mixture. Degrees Fahr.	Vapour Pressure. Lbs. per sq. in.	Air Pressure. Lbs. per sq. in.	Weight in One Cubic Foot. (Lbs.)		
			Vapour.	Air.	Total.
101.9	1.002	0.003	.00301	.000,0145	.00302
101.8	0.999	0.006	.00300	.000,029	.00303
101.0	0.975	0.030	.00293	.000,145	.00308
100.0	0.946	0.059	.00285	.000,285	.00314
95.0	0.813	0.192	.00247	.000,937	.00341
85.0	0.594	0.411	.00183	.002,044	.00388

It is possible to calculate the quantity of steam which must be condensed before the conditions represented by any line in Table I. are reached.

Thus, when the temperature is 100° Fahr. the weight of air in one cubic foot of the mixture is 0.000285 of a pound, but this originally pervaded

$$\frac{.000285}{.0000145} = 19.7 \text{ cubic feet.}$$

and was then associated with

$$19.7 \times .00301 = .05928 \text{ pound of steam.}$$

The weight of vapour condensed is therefore

$$.05928 - .00285 = .05643 \text{ pound,}$$

and this divided by 19.7 gives the weight condensed out of each cubic foot which entered.

In this way Table II. has been calculated, it shows the progress of condensation as the temperature falls, and a

column has been added to show the corresponding reduction in the volume of the air which has to be got rid of either by abstraction or by transmission farther through the condenser.

TABLE II.

Degrees Fahr	Pounds of Steam for each 1,000 Cubic Feet entering		Cubic Feet of Air for each 1000 Cubic Feet entering
	Condensed Water	Uncondensed Vapour	
101.9	0	3.01	1,000
101.8	1.51	1.50	500
101.0	2.72	0.29	100
100.0	2.86	0.145	51
95.0	2.97	0.038	15.5
85.0	2.996	0.013	7.1

For comparison with the above, similar calculations have been made for the same proportion of air but for a lower vacuum, namely, an absolute pressure of 1.509 pounds per square inch. The results have been modified to refer to the same weight of exhaust steam in the two cases and columns have been added to show the quantity of heat given up by the steam. In accordance with the assumption that the water of condensation is removed as soon as it is formed, the heat given up is calculated from the latent heat only. The heat abstracted from the air is negligible. The results for the two cases are placed side by side in Table III.

TABLE III.

Pressure=1.005 lbs. per square inch. Vac. (30 inch Bar)=27.95 inches. Temp corresponding to Pressure = 102 degrees Fahr. Air per pound of Exhaust Steam = .0048 lb				Pressure=1.509 lbs. per square inch. Vac. (30 inch Bar) = 26.93 inches. Temp. corresponding to Pressure = 118 degrees Fahr. Air per pound of Exhaust Steam = .0048 lb.			
Temp of Mixture. Degrees Fahr.	Volume of Air to be abstracted (with accom- panying vapour). Cubic feet.	Heat given up. B.T.U.	Per cent. of Steam condensed.	Temp. of Mixture. Degrees Fahr.	Volume of Air to be abstracted (with accom- panying vapour). Cubic feet.	Heat given up B.T.U.	Per cent. of Steam condensed.
101.9	333	0	0	115.89	227	0	0
101.8	166	519	50.2	115.8	128	449	43.8
101.0	33.3	934	90.4	115.0	24.4	918	89.5
100.0	16.9	985	95.0	110.0	6.14	1002	97.6
95.0	5.16	1021	98.7	100.0	1.77	1021	99.5
85.0	2.36	1030	99.5				

The interaction of the air-pump and condenser can now be readily seen.

If the lowest temperature which can be maintained in the steam space is  $100^{\circ}$  Fahr. and 16.9 cubic feet of air can be abstracted for each pound of exhaust steam, then the vacuum attainable according to Table III. will be about 28 inches. If, however, only 1.77 cubic feet can be abstracted, the vacuum will fall to 27 inches.

Again, if the pump capacity is 6 cubic feet per pound, the vacuum can be regulated by the circulating water. If this water can take in the required amount of heat and maintain a temperature of  $110^{\circ}$  Fahr. at the suction pipe, the vacuum will be about 27 inches; but if it can reduce the temperature to about  $96^{\circ}$  Fahr. a 28-inch vacuum will be attainable.

In an ideal condenser, therefore, the two quantities—lowest temperature and capacity of air abstractor—form a pair; and for every such pair there corresponds one and only one vacuum for any given proportion of air in the exhaust steam.

The above tables have been compiled to illustrate the action in the condenser. They refer to only one, and that a somewhat excessive, proportion of air. For more general application the subjoined curves will be found useful. They have been calculated per pound of air entering the condenser as the volume at any temperature is directly proportional to the weight of air entering. Each curve refers to a different degree of vacuum as indicated by the value of  $t_c$  (i.e., temperature in degrees Fahr. corresponding to the vacuum). The range of vacua is thus from about 28 to 29 inches.

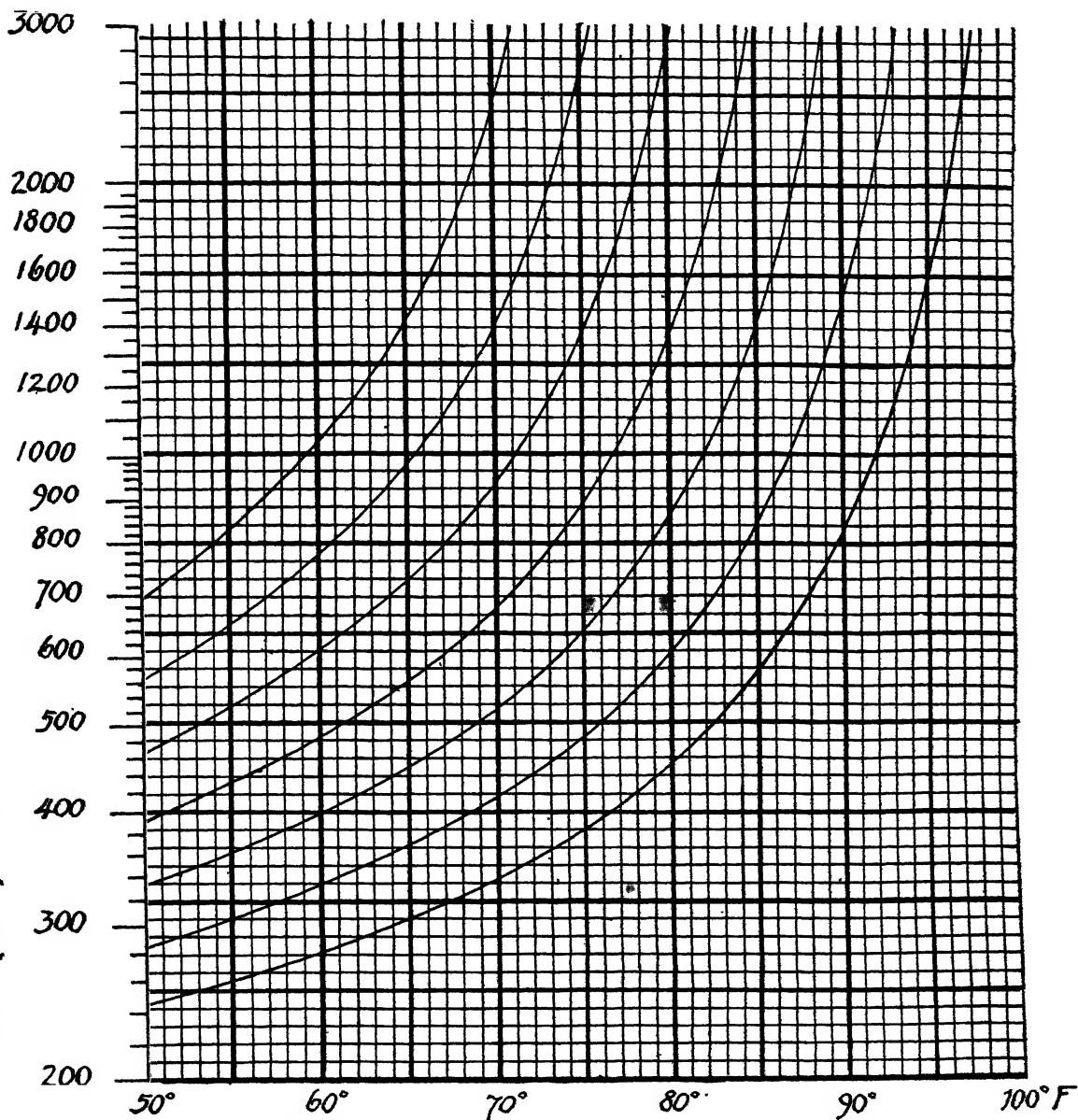
It will be seen that under certain circumstances an increase of the capacity of air-pump makes little difference to the vacuum, whereas a decrease in the temperature of the air leaving the condenser has a most beneficial effect. Under other circumstances the reverse is true; and between these extremes there is every possible combination in which temperature and pump capacity are more or less effective.







VOLUME (Cu.ft.) TO BE ABSTRACTED FOR EACH POUND OF AIR ENTERING CONDENSER.



TEMPERATURE AT WHICH AIR AND VAPOUR ARE ABSTRACTED



VARIATIONS IN THE AMOUNT OF FAT IN MILK  
DUE TO VARIATIONS IN THE TIMES  
OF MILKING.

By S. H. COLLINS.

[Read February 2nd, 1911.]

It is very well known that afternoon milk is richer in fat than morning milk. Many experiments have been made during the last few years by the Agricultural Departments of Colleges and County Councils on the composition of milk when the intervals of milking vary. These investigations have not till now been co-ordinated, but I have attempted in the following paper to collect them together and find an underlying principle that will unite them all under one rule. The data have been obtained from Chelmsford, Edinburgh, Leeds and Newcastle.

Inspection of the data showed that whilst great variations occurred in the composition of the milk, the difference between morning and evening milk varied with the inequality of the intervals of milking.

The data were arranged into groups and the results expressed as follows:—

- (1) When the intervals between milking are about 12 and 12 hours, for example, cows milked at 6 a.m. and 6 p.m., then the morning fat exceeds evening fat by  $\cdot 18$  per cent. on the average of 22 tests.
- (2) When the intervals between milking are about 13 and 11 hours, for example, cows milked at 6 a.m. and 5 p.m., then the evening fat exceeds morning fat by  $\cdot 33$  per cent., on the average of 192 tests.
- (3) When the intervals between milking are about 14 and 10 hours, for example, cows milked at 6 a.m.

and 4 p.m., then the evening fat exceeds morning fat by .70 per cent., on the average of 18 tests.

- (4) When the intervals between milking are about  $14\frac{1}{2}$  and  $9\frac{1}{2}$  hours, for example, cows milked at 6 a.m. and 3.30 p.m., then the evening fat exceeds morning fat by 1.09, on the average of 391 tests.

If we represent the interval of time from the evening milking to the morning milking by the symbol  $c$ , the interval of time from the morning milking to the evening milking by the symbol,  $m$ , the percentage of fat in the evening milk by  $E$  and the percentage of fat in the morning milk by  $M$ , then

$$E - M = \frac{c - m}{4} - .2$$

giving for the above data:—

- |     |                                      |          |          |                    |        |
|-----|--------------------------------------|----------|----------|--------------------|--------|
| (1) | (12 - 12 )                           | ÷ 4 - .2 | = - .2   | against that found | - .18  |
| (2) | (13 - 11 )                           | ÷ 4 - .2 | = + .3   | „ „                | + .33  |
| (3) | (14 - 10 )                           | ÷ 4 - .2 | = + .8   | „ „                | + .70  |
| (4) | ( $14\frac{1}{2}$ - $9\frac{1}{2}$ ) | ÷ 4 - .2 | = + 1.05 | „ „                | + 1.09 |

Although there is nothing new in the general principles given above, the quantitative representation is new, and leads to many important results. It follows that if a dairy farmer were to milk his herd 12 minutes earlier in the morning and 12 minutes later in the evening, then the milk would be 0.1 per cent. fat richer in the morning and correspondingly poorer in the evening. An important source of error in dairy experiments also becomes clear, since it is difficult to adhere to time so closely as is here shown desirable.

The above rule is only true for the average of large numbers. One day's milk of a herd of cows usually gives results which nearly conform to the rule, but one day's milk of one cow is too variable in composition to conform to any rule. The rule has proved useful in practice for detecting both adulteration and bad sampling.

# University of Durham Philosophical Society

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## REPORT FOR SESSION, 1909-10.

[10th November, 1910.]

The membership of the Society rose during the session from 137 to 180, the increase being chiefly in the undergraduate membership.

In consequence of the state of the finances some economies are recommended and a new Reserve Fund has been established. To this fund several subscriptions, amounting to about £40, have already been given or promised. It is hoped that this sum will be considerably augmented now that the existence of the fund is more widely known.

Arrangements have been made for the publication of two issues of the *Proceedings* annually. During the session Parts 4 and 5 of Vol. III. of the *Proceedings* were published, thus completing the volume which covers the period 1906-1910.

The *Proceedings* are now regularly abstracted in *Science Abstracts*, and several of the papers have been reproduced (with due acknowledgment) in other periodicals.

The work of the Boulders Committee has been continued and, in accordance with a request of the British Association, the publications of this committee are now incorporated *in extenso* in the Report of the Association.

The *Proceedings* of the Society are circulated amongst about seventy universities, learned societies, and libraries both in this country and abroad and, in exchange, a large number of valuable publications are received.

A committee has been formed for the purpose of zoning the carboniferous limestone rocks of Northumberland and Durham.

# Balance Sheet for the Session 1909=10.

INCOME.		EXPENDITURE.	
	£ s. d.		£ s. d.
To Balance from Session 1908-9 ...	11 3 4	By Expenses of Holding Meetings ...	16 19 6
„ Reserve Fund ..	10 0 0	„ Issuing Notices, Clerical, etc. ...	8 17 10
„ Bank Interest ...	1 1 0	„ Stationery ..	4 6 0
„ Grant from Armstrong College Library Committee ...	5 0 0	„ Assistant Treasurer's Commission ...	1 0 0
„ Sale of Process Book ...	0 4 6	„ Printing Proceedings, Vol. III., Pt. 4 ...	13 14 5
„ Sale of Memoir No. 1 ...	2 5 6	„ „ „ Vol. III., Pt. 5 ...	40 3 6
„ Sale of Proceedings ...	1 0 9	„ „ „ Authors' Reprints ...	8 9 6
„ Sale of Authors' Reprints ...	8 9 6		
„ 2 Subscriptions, 1908-9 ...	} 37 10 0		
„ 146 „ 1909-10 ...			
„ 2 „ 1910-11 ...			
„ Deficit ...	16 16 2		
	<u>£93 10 9</u>		<u>£93 10 9</u>

J. A. SMYTHE,

Hon. Treasurer.

Audited and found correct,

C. M. JESSOP.

November 28th, 1910.

# UNIVERSITY OF DURHAM PHILOSOPHICAL SOCIETY.

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## A NEW STEAM TRAP.

By E. M. EDEN.

[Read December 8th, 1910.]

A steam trap is an automatic valve for discharging water and air from steam pipes, separators, steam jackets, etc.

The ordinary expansion or thermostatic steam trap opens its discharge valve when the temperature of the steam or water is below a certain critical temperature depending on the adjustment of the trap. If such a trap is adjusted so that its critical temperature is but little lower than the steam temperature, it will be liable to waste steam if the steam pressure should drop slightly from any cause, as the steam would then not be hot enough to keep the valve closed. If on the other hand it is adjusted so that its critical temperature is low, it will not waste steam, but water will not be discharged until it has been cooled below the low critical temperature. In either case the opening of the valve does not depend on the amount of water which may be present in the separator, but on its temperature. If the temperature of the water to be discharged is only slightly lower than the critical temperature the valve opening will be very small and the discharge a mere dribble.

The new steam trap is shown diagrammatically in Figs. 1 and 2. The casing C is connected by the pipe P to the steam-pipe or separator to be drained so that the pressure in the casing is always the same as the pressure in the pipe to be drained. Inside the casing and entirely surrounded



by the contents of the casing is a collapsible thin metal chamber D which is connected to the discharge-valve V, so that if the chamber collapses the valve will be opened. The chamber contains only a few drops of water and is hermetically closed. The few drops of water form a film on the inside surface of the chamber, the rest of the space inside the chamber containing water vapour. The exact amount of water present is not important but there must be sufficient to fill the whole chamber with high pressure steam if evaporated.

The pressure generated inside the collapsible chamber by the partial evaporation of the film of water depends entirely on the temperature of the surrounding fluid in the casing. The upward pull on the valve depends on the difference between the external and internal pressures on the chamber.

A collapsible chamber arranged in this way has this peculiar property—so long as it is surrounded by saturated steam at any pressure it remains in equilibrium, that is, it has no tendency to collapse or expand, and under these conditions the valve remains shut, Fig. 1. This is strictly true, whatever the pressure of the steam may be; for example, if the steam pressure is atmospheric its temperature is  $212^{\circ}$  F., and the collapsible chamber being surrounded by steam at  $212^{\circ}$ , its temperature is or very rapidly becomes  $212^{\circ}$  also, and the pressure of steam generated inside the chamber is atmospheric, the same as the external pressure. Again, if the steam pressure is 200 lbs. per square inch, its temperature is  $387^{\circ}$  F. and the pressure generated inside the collapsible chamber is also 200 lbs. per square inch. So that in either case, with steam in the trap, the chamber is in equilibrium and the valve remains shut.

If however, the trap contains water or air only a few degrees cooler than saturated steam at the same pressure, the pressure generated inside the collapsible chamber will not be so great as the pressure outside, and the chamber

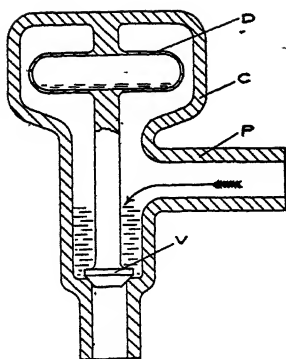


FIGURE 1

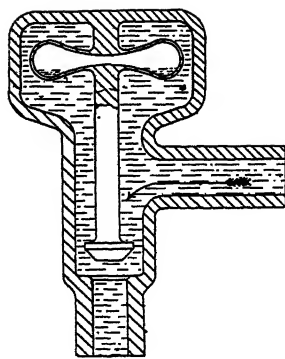


FIGURE 2

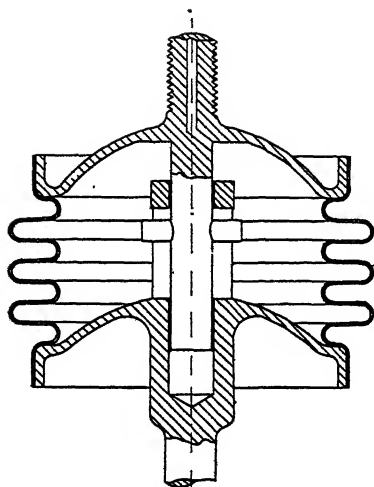


FIGURE 3

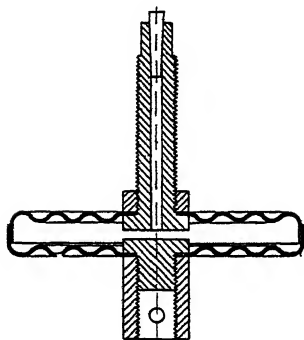


FIGURE 4

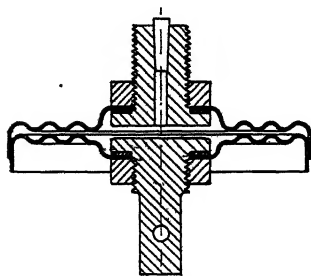


FIGURE 5

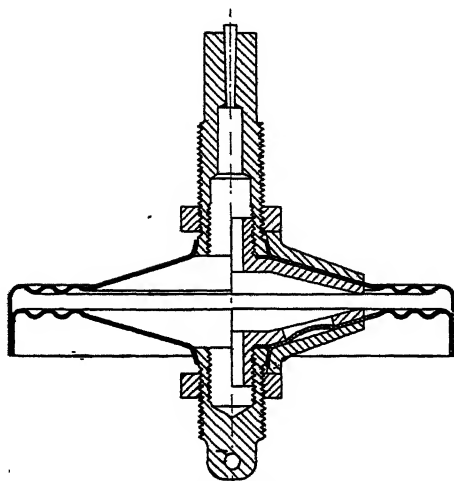


FIGURE 6

will collapse lifting the valve off its seat, Fig. 2. For example, if the steam pressure is 200 lbs. per square inch, and the trap contains water at a temperature of  $382^{\circ}$  F., only  $5^{\circ}$  less than saturated steam at 200 lbs. pressure, the pressure generated in the collapsible chamber will be only 185 lbs. per square inch, and the 15 lbs. per square inch, excess pressure outside the chamber, will be sufficient to lift the discharge valve off its seat.

It will be seen that the temperature at which the water is discharged is not fixed, as is the case with a thermostatic trap, but varies automatically with the steam pressure so as to be always a few degrees only cooler than the steam. No adjustment whatever is required for different pressures and the condensation from the steam pipes is discharged in quantity even when very hot.

A steam trap on this principle can be made much more "powerful" than either an expansion or float trap of anything like the same size, as the energy available for controlling the valve is comparatively large. Assuming an effective diameter of collapsible chamber of 3 inches and 200 lbs. steam pressure, water entering the trap only  $5^{\circ}$  cooler than saturated steam would cause an upward pull on the valve of 106 lbs. which would be sufficient to lift a  $\frac{3}{4}$ -inch valve off its seat. At low pressures the available force is less, but the pull required to lift the valve is also less, so that a  $5^{\circ}$  drop in temperature would still be sufficient to lift the  $\frac{3}{4}$ -inch valve. The lift of the valve would depend on the flexibility of the collapsible chamber.

The design and construction of a reliable collapsible chamber for high pressure work is not an easy matter, it has to stand a possible external pressure of 200 or 300 lbs. per square inch, and the full steam temperature without damage, and yet it must be sufficiently flexible to give a large valve lift with a small difference of pressure, say, 10 lbs. per square inch.

The available energy for working the valve = the pressure difference  $\times \frac{1}{2}$  change in volume of the chamber, so

that the best form would be the one which gives the largest change in volume with the smallest difference of pressure.

On account of the small change of volume the Bourdon tube is not a suitable form. Probably the best form for the collapsible chamber would be like a concertina or Japanese lantern, as shown in Fig. 3, with internal stops to limit the contraction and expansion. Such a form would give a large change of volume for a small pressure difference and at the same time, owing to the internal stops, would be capable of standing a very large pressure difference without damage. Unfortunately the thin metal corrugated cylinder is not easy to produce experimentally and no attempt has been made to make a collapsible chamber of this form.

The author has made a large number of experimentally collapsible chambers of various patterns, but all modifications of the form used in the aneroid barometer made of two corrugated diaphragms fastened together to form a hollow box. The earliest diaphragms were stamped from dies but it was soon found that a much harder material could be used by spinning, and the forms shown in Figs. 4, 5, and 6 were all produced by spinning.

The material used for the diaphragms has nearly always been a hard rolled tough German silver, which appears to retain its springiness when heated to high pressure steam temperatures better than either brass or bronze. Some of the early forms were made like Fig. 4, the two halves being brazed together and the studs brazed to the spinnings. Owing to the heat to which they were subjected in brazing, these diaphragms were quite soft and were undoubtedly stressed beyond the elastic limit when at work. Various forms of mechanical joint were tried for connecting the two diaphragms together, but it was not found practicable to produce a reliable joint except by brazing or silver soldering.

Fig. 5 shows a later form. The projecting edges are silver soldered with an oxygen blow-pipe, while the rest of the diaphragm chamber is kept cool, thus avoiding the

softening of the diaphragms. The joint also is not likely to be strained by the working of the diaphragms. The joint between the studs and the diaphragms is metallic by means of copper washers, the studs being of tool steel and the nuts screwed up hard until the heads become convex. These joints are made before the two diaphragms are soldered together.

When the trap is at work the collapsible chamber is only subjected to sufficient pressure to enable it to lift the valve,

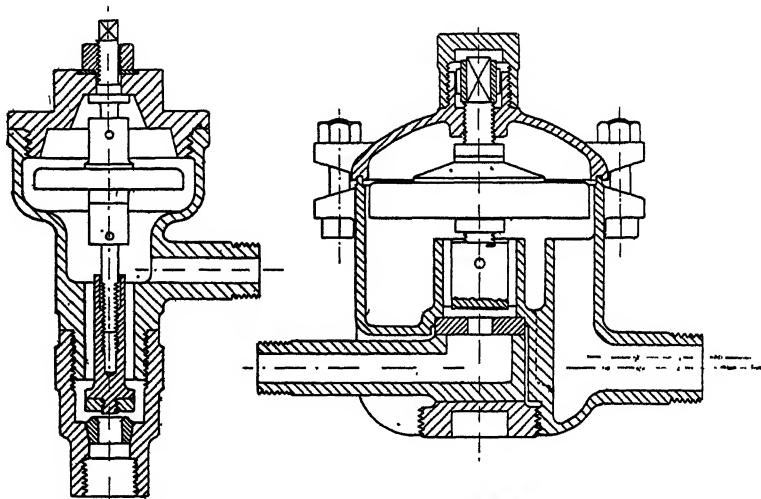


FIGURE 7.

FIGURE 8.

but if the trap is discharging quite cold water, and the outlet of the trap is throttled it is possible that the collapsible chamber may have to withstand a very high cold water pressure.

In the collapsible chamber of Fig. 5 the space inside, when collapsed, is made as small as possible and when the heavy external pressure comes on the outside the diaphragms bed on solid water forming a water cushion so that the metal is perfectly safe against any external pressure.

Fig. 7 shows a simple form of trap with a collapsible chamber of this form. The trap is adjusted so that the

valve is open by two or three turns of the adjusting screw when cold, the trap will then work correctly at any pressure. The exact adjustment is not important, but if the valve is adjusted too low the valve lift is reduced, if much too high the valve will not close for low-pressure steam.

If for any reason the steam trap should contain superheated instead of saturated steam, the pressure generated in the collapsible chamber will be greater than the external pressure and the chamber will tend to blow out. If the trap contains only high-pressure steam and the pressure is suddenly reduced to atmospheric pressure (by shutting off the boiler supply and blowing the steam out of the pipes) the pressure outside the collapsible chamber will become atmospheric, but the whole trap and its contents will be left at the high steam temperature.

Under these conditions it is possible that the collapsible chamber may have to stand an unbalanced internal pressure equal to the maximum steam pressure in the steam pipes. The diaphragms of Fig. 5, which were  $2\frac{1}{4}$  inches diameter and about  $\frac{1}{16}$  inch thick, were quite unable to stand the excessive superheat and several were burst from this cause. To get over this difficulty later traps were arranged with a "puddle" under the diaphragm which always contained water; if the pressure drops suddenly the water in the puddle boils rapidly and cools down the diaphragm and the trap casing.

Fig. 8 shows a larger trap with a  $3\frac{1}{4}$ -inch diaphragm chamber and a nickel steel valve and seat. The construction of the collapsible chamber is shown to a larger scale in Fig. 6, the central portion of the diaphragm is reinforced with internal and external conical discs and the metallic joints are done away with, the hollow gun-metal studs being silver soldered to the diaphragms with the oxygen blow-pipe. The silver soldering softens the centre of the diaphragm, but this portion is protected by the conical discs. The trap, Fig. 8, has a very large "puddle." The first diaphragms were made without the external conical discs and the "puddle" did not

keep down the superheat sufficiently to save them from blowing out. With the external reinforcements to the diaphragm the "puddle" is probably unnecessary.

The collapsible chamber of Fig. 6 is not considered to be a satisfactory design as it is too elaborate and expensive to make, and does not work any better if as well as some of the early forms.

## ON THE MUTUAL DEVELOPMENTS OF METALLURGY AND ENGINEERING.

By Prof. HENRY LOUIS.

[Read February 9th, 1911.]

Anyone who has followed the history of technology at all cannot fail to be struck with the rapid increase in the employment of metals that has characterised the latter half of the nineteenth century, and which is going on fully as rapidly in the twentieth. In no branch of technology is this more evident than in engineering; iron and steel have taken the place of wood, leather, hemp, etc., and even stone is being replaced in part by structural steel, and in part by one of the most recent applications of iron in the form of ferro-concrete. In the same way the recent great developments in the application of electricity have led to a far more extended use of copper. Metals are so largely used in conjunction with each other that any extension in the use of one leads to the greater employment of others, so that the development of metallurgy takes place all round, more or less simultaneously. Of late years it may fairly be said that the history of metallurgy is the history of technology at large, but this would by no means be true of earlier periods, and it should be interesting to trace how this close connection has gradually developed from its early beginnings.

We have no records of the dawn of the metallurgical

industry; we know that a copper age preceded a bronze age, and the latter an iron age, although there is little doubt that these periods largely overlapped. There are many reasons why copper should have been one of the first metals to have been impressed into the service of man, and it was probably first by accident and afterwards by design that tin was added to it to improve certain of its useful qualities; it is also probable that the introduction of iron would have come at a somewhat later period. The Greeks and Romans were already skilled metal workers, and metallurgy had under them reached already a relatively high stage of development. In same respects, however, differentiation had not proceeded very far in this industry. It seems to be generally admitted that the Greek *μεταλλον* is derived from the word *ἀλειν*, to seek for, so that in these early days the metallurgist was what we should now call a prospector, a man who sought for ore, and when he found it, no doubt worked and smelted it himself. Few people seem to realise how rudimentary the appliances may be in which successful smelting can be conducted. A hole in the ground makes an efficient furnace and this, with a blast pipe of any kind connected with some form of a bellows, is all that is needed to smelt any of the commoner metals.

Even at the present day we meet with such metallurgical appliances in remote parts of the world. Thus the Japanese use, or quite recently used, a furnace such as I have described for smelting tin and copper. No doubt quite at the first smelting was conducted in such holes in the ground to which no artificial blast was applied, such as we know was the case with some of the early methods of lead smelting in our own country, even after Roman times.<sup>1</sup> Long before this period the efficacy of artificial blast must have been discovered, and this pre-historic invention may be said to have been one of the first great metallurgical improvements. It must have been a very old one; it seems to be fully proved that the

<sup>1</sup> According to Joshua Childrey, this practice continued into the seventeenth century (*Britannia Baconica*, London, 1661).



Assyrians were not only well acquainted with iron but had attained some considerable skill in its manufacture, having advanced far enough to make chain mail; thus as far back as 900 years B.C. iron manufacture had long passed the rudimentary stages. I need hardly say that in all these early methods of smelting, wood and charcoal were the only fuels employed and continued to be so for many centuries. The iron produced by them was never cast iron but was always malleable iron, which is necessarily obtained when iron ore is reduced in a shallow furnace with charcoal as fuel, where the temperature attained is relatively low.

Probably long before Roman times the iron smelting furnace was a built-up furnace five or six feet high, the front wall of which would be wholly or partly taken down to allow the lump of malleable iron produced by smelting to be taken out; furnaces such as these are still in use in India, Africa, Brazil, etc., at the present day. Iron appears to have been made pretty well all over Europe in Roman times; it seems certain that it was made in this country, before the time of the Roman Conquest, and there is no doubt that its manufacture extended considerably during the Roman occupation, when it was made as far south as the Wealds of Sussex, and as far North as the banks of the Tyne. Southern Germany was known as an important seat of iron manufacture even in Cæsar's day, and it appears to have long retained its importance.

The only other common metals known to the Ancients were lead, copper, and tin, all of which are easily reduced from their ores; brass was known for a very long time before it was discovered that zinc was one of its constituents, it being always made direct from zinc ore; Roman brass coins have been analysed and found to contain over 25 per cent. of zinc, so that the material was certainly known to them, although they were ignorant of its true composition. The metallurgy of lead was relatively far advanced; quite a number of pieces of lead of Roman age have been found

in this country, the earliest date about 44 A.D.,<sup>2</sup> and several of these are marked "EX. ARG." or desilverised; it is also evident from the composition of articles of Roman lead that the metallurgists of that day were tolerably well advanced with their methods of desilverisation. In Roman times lead was obtained from Spain and Great Britain,<sup>3</sup> tin chiefly it would seem from this country, and copper from Southern Europe. Whilst metallurgy had thus reached a certain stage of development, it had not yet become of much use to the engineer. Perhaps lead was the first of all the metals to be applied to any kind of engineering use; the Romans used lead pipes for water conduits, and also made use of sheet lead. As an engineering curiosity I may mention that at Pompei a piece of rope made of bronze wires has been discovered. Practically speaking, however, the Roman engineer made no use of the metals.

The position of Engineering at this time is somewhat more difficult to define; it may be questioned whether any civil engineering at all existed, most of what we would now call civil engineering works, such as road making, bridge building, construction of aqueducts, etc., having been really undertaken for military purposes; in all this work metallurgy played a very unimportant part.

Mechanical engineering was still in a rudimentary state, the patient labour and manual skill of the artificer occupying the place that has since been filled by machine tools.

The earliest of any of these was probably the potter's wheel, known to have existed as early as 4000 B.C. This probably gave rise to the lathe, and the Egyptians used the lathe—probably a form of dead-centre pole lathe, for turning as well as bow-drills for drilling stone, wood and similar materials. The lathe was well known to the Romans, and they probably used it for metal work. It seems impossible to discover when screws were first used; Popps, in the fourth century, describes the setting out and chasing of screws by

<sup>2</sup> *The Archaeological Journal*, vol. xvi., 1859.

<sup>3</sup> Pliny, Lib. xxxiv.

hand, but, upon the whole, engineering at the commencement of our era was probably more backward than metallurgy.

There are but scanty records of metallurgical progress in the earlier centuries; the metallurgist was still no doubt a rude worker, half miner and half smelter, who practised his empirical art without the desire or the ability to put his methods on paper, so that our views on this subject depend mainly on inference and conjecture.

It seems likely that the most rapid advances were made in the metallurgy of iron, probably due to its importance for arms and armour. No doubt progress in iron smelting consisted in making the furnaces gradually larger. It is said that in 1323 the furnace bellows were for the first time worked by means of a water wheel, though hand-worked bellows were in use long after that time. It was about this time that the *Stückofen* *Bauernofen* or *Blaseofen* of the Germans was in use for iron smelting, and this was some 10 feet in height. Similar progress was also being made in Sweden, which was already known in the seventh century as the "Motherland of iron;" there, a similar furnace called the "*Osmund*" or lump furnace was employed, which produced lumps of iron; these were hammered into rough bars known in trade as "*Osmundsern*," in which form they were exported.

Gradually the size of these furnaces grew, as larger and larger bars of iron were required. It is quite possible that the invention of gunpowder early in the fourteenth century played some part in this demand.

The first cannon were cast of bronze, but this was soon found to be too weak, and then cannon made of wrought iron bars hooped together were introduced, of which *Mons Meg* in Edinburgh, made in 1455, is a noted example. A wholly unexpected result followed this increase in the size of the furnaces; when the furnaces had attained a certain size and the fire in them was urged by powerful bellows, the temperature rose above that at which carbon and iron combine, and the result was that molten iron—cast-iron—or pig-iron was produced. The date and place are very uncer-

tain, and nothing at all is known as to the discoverer, but there seems little doubt that cast-iron was produced in the fourteenth century, though I believe that the first writer who definitely refers to cast-iron was Lazarus Ercker whose work "Aula Subterranea" was published in 1574. Agricola,<sup>4</sup> writing in 1561, knew that iron could be fused, but had to make his fusible iron by special methods. No doubt at first this production of cast-iron was a source of trouble to iron-workers, to whom this relatively brittle material would be of little value.

Probably it was not long before it was discovered that this cast-iron could be rendered malleable or "freshened up," to use the old German phrase, by heating it in a forge, like the old shallow iron smelting furnace; this invention very probably originated in Germany, whence it was introduced into Sweden about the year 1600. It must not be supposed that the manufacture of cast-iron at once displaced entirely the direct production of wrought iron from the ore, for the latter process continued in use in Spain, where it was called the Catalan process, up to about 1870. Even in this country the method was used in the Furness district of Lancashire in the year 1674, as appears from a very interesting description in the Philosophical Transactions.<sup>5</sup> It may be noted that it is in this same district that the only charcoal furnace in Great Britain has survived until the present day, namely, at Backbarrow. Meantime some uses had been found for cast-iron; cast-iron cannon balls are said to have been made at Memingen in 1388; in 1412 small cannon were cast at Lille; in Britain cast-iron guns were first made in Sussex in 1543, and rapidly attained considerable size. There seems little doubt that by this time iron manufacture had developed very rapidly in this country, so much so that the destruction of the forests for the production of charcoal was beginning to excite attention, probably owing to the fear lest the supply of oak wood for shipbuilding might be affected.

<sup>4</sup> *De re Metallica*, Lib. ix.

<sup>5</sup> *Phil. Trans.*, 1692, No. 199. (Letters from Mr. John Sturdie.)

In the first year of Queen Elizabeth's reign (1558) and again in 1584, Acts were passed for the preservation of timber and to limit the erection of new ironworks. About this time the first attempts were made to smelt iron by means of coal; the same had already been tried in the case of other metals; Cardinal Wolsey seems to have been among the first to make such an attempt, which he did at the great furnace for lead-smelting which he had had built at Gateshead-on-Tyne; the attempt seems to have been a failure, for we learn that in 1527 he disposed of his furnace to one Thomas Wynter. It seems clear that no great progress was made, seeing that in 1678 a patent was granted to Viscount Grandison for smelting lead ore in a reverberatory furnace with seacoal. In 1692, under a Charter of William and Mary there was founded the famous London Lead Company, the proper title of which was "The governor and Company for smelting down lead with Pit coal and Sea coal," and it is noteworthy that this Company carried on lead smelting operations continuously until it was finally wound up in 1905. According to Pryce<sup>6</sup> the reverberatory furnace was first used for tin and copper smelting in 1705, thus rendering it possible to use coal in the place of wood for these operations. It is interesting to note that by this time the two arts of mining and metallurgy were beginning to be differentiated, for Pryce tells us that the tin miner or "Tinner" took his tin ore to the blowing house to have it smelted. The need of using coal seems to have become more urgent in the case of iron, due, perhaps, to the fact that the ironworks of Sussex were so much nearer the Capital than were the lead, copper or tin smelting works. It seems that the first patent for smelting iron with seacoal or pit coal was granted to Simon Sturtevant in 1611; it is conjectured that he tried to use some sort of reverberatory furnace, but this is not clear; at any rate his attempt seems to have failed. In 1619 another patent was granted to Dud Dudley, a natural

<sup>6</sup> *Mineralogia Cornubiensis.*

son of Lord Dudley, who certainly attained some measure of success. He built two furnaces in Staffordshire, and records that he made as much as 7 tons a week in one of them. His success was not, however, sufficiently marked to induce others to follow his example, for we read in the *Philosophical Transactions* for 1677<sup>7</sup> that in the Forest of Dean charcoal furnaces 30 feet high were in use, and that various attempts had been made to substitute coal, all of which had failed. The first really successful introduction was due to Abraham Darby of Colebrook Dale in Shropshire in 1735. He hit on the idea of treating coal like the charcoal burner treated wood, and with the coke thus made he succeeded in smelting iron. He also appears to have been the first to successfully cast hollow-ware of iron, thus replacing brass by cast-iron. The Colebrooke Dale Works still holds to-day a high position amongst iron founders; they appear to have been the first to use a steam engine, and they were the first to construct a cast-iron bridge over the Severn about 1785. Up to this time, brass had been the general material from which ordinary castings were made; some of these were quite large, *e.g.*, the brass guns of the "May Rose," sunk in 1545, which were 11 feet in length. All the brass used at this time was calamine brass, the manufacture of which has been described by many old writers, as, for example, by Lazarus Ercker in 1574;<sup>8</sup> he describes how 8 small crucibles are set in a fire, each being charged with a scoop full of mixed calamine and charcoal, on top of which was placed 8 lbs. of bean shot copper. The crucibles are closed and strongly heated, after which the molten brass is poured out. Ercker notes that each charge of copper gains 1 lb. in weight in the operation. He distinguishes between furnace calamine and natural calamine, as did Pliny long before him, and both point out that either material may be used in brass making.<sup>9</sup> Until the middle of the century

<sup>7</sup> *Phil. Trans.*, No. 137.

<sup>8</sup> *Aula Subterranea*.

<sup>9</sup> Thomas Povey describes the process in practically the same way in 1693. *Phil. Trans.*, 1693, No. 200.

brass seems to have been made mainly in Flanders and in Central Germany; it was largely imported into this country from Cologne, in rectangular pieces, called Cullen plates. It is well known that Queen Elizabeth was active in getting German miners and metallurgists over to this country in order to teach British workers the more advanced German methods, and in the years 1565 to 1568 she granted patents to several people, amongst whom German names are conspicuous, for searching for calamine, and for manufacturing latten or brass. From this time onwards brass making became a British industry, which rose to importance between 1700 and 1750.

It is doubtful when zinc was first discovered to be an independent metal; Paracelsus, writing in the middle of the sixteenth century, seems to have been the first to use the name zinc, but he was by no means clear as to its application; it is said that zinc was imported from China in the seventeenth century, when it seems to have been called also "spauter." Boyle seems to have discovered that brass could be made by smelting copper and zinc together, but writers even at the beginning of the eighteenth century classed zinc not as a metal but as a "semi metal," and Homberg, writing in 1710, considered it to be a natural mixture of tin and iron, so that it was evidently not until about the middle of the eighteenth century that its true nature began to be understood. There are various patents relating to its distillation from calamine about the year 1742, when it seems to have been smelted in Sweden. It is probable that it was really smelted before this time in Saxony, which was throughout the middle ages the cradle of mining and metallurgy; German miners travelled to England, to Hungary, and to Sweden, to instruct the natives in these various countries, perhaps especially in the art of blasting, which was a German invention, and they have left profound traces of their language, customs, and even their superstitions, as witness the names nickel and cobalt, in every branch of metallurgical work.

As regards steel, it was early discovered, probably in pre-Roman times, that iron could be made exceptionally hard by treating it in special ways, and certain ores were celebrated as producing iron of steely quality, but the reason seems to have long remained unsuspected. The Romans only knew that certain ores gave steely iron; thus the iron from Noricum was celebrated for this property, this region corresponding to Styria, which produces manganiferous iron ore, suitable for direct steel manufacture. Biringuccio<sup>1</sup> in 1540 and Agricola<sup>2</sup> in 1561 published accounts of a method of making steel by keeping lumps of wrought iron immersed for some hours in molten cast iron, and Dr. Martin Lister repeats a similar account in 1693.<sup>3</sup> It is probable that the method of making steel that consists in keeping bars of iron heated to redness in charcoal (the process of "cementing") is an ancient one, though the first record of it appears to be a very complete description by Reamur in 1722 of the process as it was then practised. All the better class of steel was made in this way, and the first recorded great improvement in the quality of steel was brought about by the fusion of this cement steel in crucibles, by Benjamin Huntsman in 1750, which laid the foundation of the pre-eminence of Sheffield in the steel trade. By this improvement high class steel for tools, springs, etc., was produced, though the rationale of the process seems to have remained obscure.

Meantime we find but few records of engineering progress, the temptation to record these being but slight, and the knowledge of engineering being largely confined to those whose taste did not lie in the direction of literature. We may note that the first application of mechanical engineering to the working of metals was probably the helve or tilt-hammer; then came the drawing of wire by hand through a draw-plate, which seems to have originated about 1550; the draw-bench for drawing on to a revolving cylinder, seems to have come quite a century later, and was not introduced into England until 1565.

<sup>1</sup> *De la Pirotechnia.*    <sup>2</sup> *De re metallica.*    <sup>3</sup> *Phil. Trans.*, 1693, No. 293.



Flatting mills for flattening out wires were invented in Germany, quite possibly in Nuremberg, about the fifteenth century, but this method of working was long kept secret. An invention, important rather for what it led to than in itself, was that of rolling sheet lead instead of casting it; we find that in 1670 an Act was passed giving the privilege of this new invention to Sir Philip Howard & Company. Of mechanical tools we find that the turning lathe underwent many improvements about this time, which are described in a work by Hartmann Schopper, dated 1548; the screw-cutting lathe was certainly known to Jacques Besson in 1569; a rude form of slide-rest appears to have been known already in 1648, though it was not properly described until 1772. It was re-invented in England by Maudslay in 1794, from which time machine-tools proper may be said to date. It will be remembered that Maudslay also greatly improved screw cutting, and was the first to make really accurate screws in 1800-1810.

It would thus seem that in the early part of the eighteenth century metallurgy was fairly well advanced, though the advances were purely empirical; in this country and probably in this country only, coal was beginning to replace wood as a fuel, and for the first time England began to take a commanding lead in the metallurgical industries; metals were, however, hardly used in any branch of engineering other than military, if indeed any other branches of engineering can be said to have truly existed. Then came the epoch-making invention which distinguishes the eighteenth century, and which brought metallurgy and general technology for the first time into intimate union. Up to that time man had been able to make use only of kinetic energy, the motion of water, of air, and of animal muscle, as sources of power. The genius of Newcomen and of Watt then taught him how to utilise the latent energy of fuel for the same purposes. Whatever wonderful inventions future ages may have in store, it seems probable that none will ever produce a more profound modification than

did this one in all methods of technology. Between the periods of Newcomen's first engine, 1712, and Watt's patent, 1769, iron smelting with coal had been accomplished, so that by the time that the steam engine with its requirements of a strong material, capable of standing a high temperature, had been designed by the engineer, the metallurgist was able to furnish an ample supply of iron to meet his needs.

From this time onwards the history of metallurgy, or at any rate of the metallurgy of iron, is the history of engineering, and each advance in the one branch corresponds with a step in the other. Soon after this, what may fairly be called the foundation of scientific metallurgy was laid; corresponding with the general development of chemistry that was then taking place, the chemistry of iron also received attention. It seems to be generally admitted that Bergman, whose *Opuscula Chemica et Physica* were published in 1788, after his death, was the first to show that steel and cast-iron differed from wrought iron only by containing larger proportions of carbon, and that these two former substances were really carbides of iron. He also proved that cold-shortness in iron was due to a phosphuret of iron. Rinman and Morveau also did work in this direction, and Frederick Accum's *System of Theoretical and Practical Chemistry*, published in London in 1803, shows a very considerable knowledge of the chemistry of iron smelting, puddling, converting, etc. Thus the scientific basis of metallurgy was nearly contemporaneous with that of engineering. The application of the steam engine required heavier castings and forgings than had ever before been thought of, but at the same time by supplying the necessary motive power, it helped to furnish the means for their production; it will be remembered that the first blowing engine was built by James Watt for the Carron Iron Works in 1760.

The next step in the joint advancement of both branches may be said to have been the invention of the locomotive;

Trevithick seems to have built his first attempt at a working locomotive at the Coalbrook Dale Works, which it may be remembered was one of the first works to build steam engines; it also took the lead in the building of iron boats the first of which appears to have been a canal boat built by Mr. Wilkinson in 1788. Trevithick's next locomotive was built in South Wales for hauling iron for iron works. Cast-iron rails were used at first, but when the demand for something stronger arose, wrought iron began to take its place.

This change was immensely helped by the invention of puddling by Henry Cort in 1784, who thus rendered it possible to make good bar iron in large quantity without the use of charcoal, whilst he also invented the grooved rolls, used for rolling out the bars, and could thus produce easily a bar of any desired section, instead of having to employ the old laborious method of beating it into shape under a tilt hammer. From this time onward the engineer had both cast-iron and wrought iron at his disposal in masses that were continually getting larger, and the beginning of the nineteenth century was seeing the applications of steam and iron increasing day by day. A metallurgical invention that must be referred to here, was that of the application of hot blast to the blast furnace by Neilson in 1838; this enabled cast-iron to be produced in much larger quantities and at a much cheaper rate, and thus assisted the engineer, though this, like so many other improvements in metallurgical methods, was attended by a deterioration in the quality of the material.

Just about this time scientific engineering may be said to have originated, but it was not until Mushet Hodgkinson, Fairbairn, Kirkaldy and others commenced the systematic testing of iron, that data were available for engineering calculations, the results of which were soon seen in the construction of such important works as the Britannia Tubular wrought iron bridge, and in the design of iron vessels of large size; the first sea-going iron boat, the "Aaron

Mawby", was built in 1821, and soon after this, about 1835, the use of armour plate for vessels of war was proposed, the manufacture of which made fresh demands upon the iron smelter and worker.

The inception of the next important metallurgical invention, which in its turn had a most extensive influence upon civil engineering, was again due to military engineering. It was in attempting to produce a suitable material for artillery that Sir Henry Bessemer worked out his great discovery in 1856, and gave to the engineering world a new material, namely, ingot iron or mild steel. The Bessemer process was followed a few years later (1861) by the Siemens open hearth process, and these two processes together supplied the material for structural ironworks. Engineering methods soon adapted themselves to this valuable material, and with the invention of ingot iron and its application to structural purposes, modern engineering may be said to have originated. These processes could only make steel from pure non-phosphoric materials, but the Gilchrist-Thomas Basic process, in 1877, enabled it to be made from any class of ore. Important though this last named process is from the metallurgist's point of view, it is of less importance to the engineer, because it only afforded him another means of obtaining the same substance, and thus only helped him indirectly by increasing the supply of this material.

About this time steel casting attracted renewed attention, the Germans being the pioneers in the art of producing large masses of molten steel. The great firm of Frederick Krupp shewed a 2½-ton cast ingot at the International Exhibition of 1851, and already a 21-ton ingot at the 1862 Exhibition. These were high-carbon steels intended for subsequent forging. I believe that the first openhearth mild steel castings were some stamp shoes for a quartz mill cast in 1880 at Landore, where I was at that time employed.

This was a period also of great engineering progress, of high pressure steam, compound engines, huge iron

structures, powerful machine tools; the first planing machine was built by Clement in 1825, and this and other tools were greatly improved by Sir Joseph Whitworth between 1826 and 1850. A new branch of engineering, electrical engineering, arose, and with it came the twin art of electrometallurgy.

The latter part of the nineteenth century was distinguished by the first serious attempt to place metallurgy in general upon a truly scientific basis; the greatest help in this direction has been given by metallography, the study of the minute structure of metals and alloys under the microscope, a mode of research that was first suggested by Sorby in 1857; simultaneously the various forms of electric pyrometer with which the names of Siemens, Le Chatelier, and Callender are connected, enabled accurate determinations to be made of high temperatures, and thus rendered it possible to study the effects of heat treatment, and to substitute accurate scientific work for empiric methods. Another result of these studies was to place at the disposal of the engineer a number of "alloy" steels such as manganese steel, chromium steel, etc., having qualities the combination of which had hitherto been unobtainable. Metallurgy had reached this stage when, about twenty-five years ago, engineers made a demand upon it from a new quarter. Up to this time the use of these special steels had been limited by their cost. No manufacturer would use one of these expensive steels unless he could save by its use more money than the additional expenses incurred by it. At this point, the advent of the motor car changed the position; the question was no longer a strictly economic one, for the wealthy amateur began to demand the highest quality of material irrespective of its cost. This demand was met by the researches of a group of metallurgists, largely Frenchmen, who produced the special steels required for these purposes, their work again being largely assisted by the rapid development of a new metallurgical appliance, the electrical furnace. Out of these elaborate researches

again came a quite different development, namely, the invention of self-hardening and high-speed steels for machine tools, which enable machining to be performed in a fraction of the time that was previously necessary.

It will have been noted that in all the latter part of this review I have referred to the metallurgy of iron alone; it must not be supposed that no progress was made with that of the other metals, but on the one hand their part in the advancement of engineering is less important, and on the other hand the great development in their production is due quite as much to mining as to metallurgical causes. In copper the successive inventions for cheapening its production, such as the Bessemering of copper matte by Manhes in 1880, the introduction of pyritic smelting about 1890, due largely to Mr. W. L. Austin in Montana, and the electrolytic refining of copper, which was introduced by Elkington in 1865, and about thirty years later became a thoroughly practical process, all helped in cheapening the process of copper extraction, and thus enabled poorer ores to be worked on a scale of always increasing magnitude, thus keeping pace with the rapidly growing requirements of the electrician. Similar advances were made in lead smelting, in which the size of the blast furnace was gradually increased, whilst a number of new processes were successfully introduced. Again, the discovery of aluminium by Wöhler in 1827, followed some thirty years later by the cheaper methods of manufacture due to Deville, placed a new material at the disposal of the engineer, though it must be admitted that from the engineer's point of view aluminium has hitherto been found to be a disappointing metal.

The net result in every case has been that the production of all the metals has increased with immense rapidity, and it seems as though it were likely to continue to do so, whilst the scientific research that is now being devoted to their alloys, promises to render it possible to furnish the engineer with almost any combination of qualities that he may

desire. The engineer will be forced to depend more and more upon the metallurgist, because engineering designs must be limited by the possibility of obtaining materials in which these designs can be executed, and progress will only be possible in the future by the closest co-operation between the man who produces the materials and the man who is responsible for their application.

## THE DISPLACEMENT OF THE PARTICLES IN A CASE OF FLUID MOTION.

By T. H. HAVELOCK, M.A., D.Sc.

[Read March 3rd, 1911.]

The leading features of the motion induced by the passage of a cylinder through a perfect fluid are well known, but certain aspects of the permanent displacement of the fluid particles are less familiar. The following notes on these were suggested by an unexplained paradox which is mentioned in recent treatises, such as Lanchester's Aero-dynamics and Taylor's Speed and Power of Ships; it was found later that the same difficulty is mentioned by Maxwell in a paper on the paths of the particles. The present remarks are arranged as follows:—

1. From the ordinary theory of the fluid motion is deduced a simple proof of Rankine's formula for the radius of curvature of the path of a particle, and the solution is then completed in terms of elliptic functions.
2. After drawing paths of particles, curves are obtained for the subsequent positions of lines of particles which were abreast of the cylinder at certain times.
3. A graphical study of the deformation of a group of particles as it passes near the cylinder suggests a difference between the behaviour of an ideally continuous fluid and one which is molecular.

4. A discussion of the paradox that the fluid appears to have a permanent forward displacement ultimately. The difficulty is shown to arise from the introduction of infinities without precise definition of conditions. Analytically the ambiguity occurs in the form of a double integral whose value depends upon the order of performing the integrations.

1.—A circular cylinder of radius  $a$  and of infinite length moves through an infinite fluid with uniform velocity  $u$  at right angles to its axis. The fluid is assumed to be perfectly continuous, frictionless, and incompressible; and under these conditions a certain continuous motion is determined in the fluid. Let the diagram in Fig. 1 represent a section at right angles to the axis of the cylinder, the circle with centre  $O$  being a section of the cylinder at any instant.

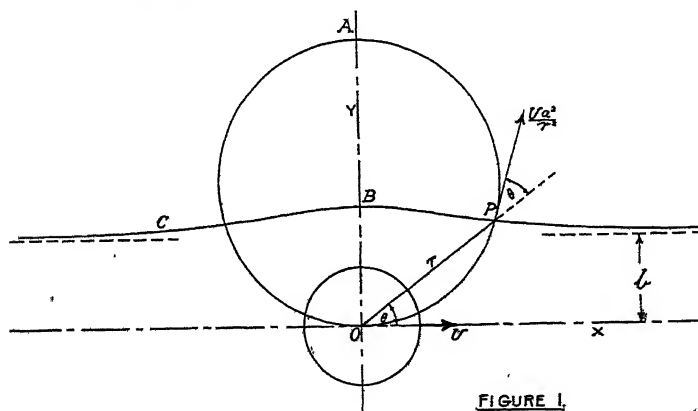


FIGURE 1.

The fluid at any point  $P(r, \theta)$  is moving with velocity  $ua^2/r^2$  in a direction making an angle  $2\theta$  with  $Ox$ , that is tangentially to a circle through  $P$  touching the axis of  $x$  at  $O$ . Thus the fluid at points on a circle such as  $OPA$  is moving tangentially to the circle at each point at a given instant. This solution gives the actual velocity of the fluid at any point at any time; it does not follow the motion of a given particle of the fluid. If we fix attention upon a fluid



particle at P in Fig. 1, we could trace its path relatively to the cylinder by superposing on its actual motion a backward velocity  $u$  parallel to  $Ox$ . It can be shown that this relative path is a curve PBC whose equation in terms of  $y$  and  $r$  is

$$y\left(1 - \frac{a^2}{r^2}\right) = b, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $b$  is the distance of the particle from the axis  $Ox$  when at an infinite distance before or behind the cylinder. These curves, given by different values of  $b$ , would be the actual paths of the fluid particles if the cylinder were at rest and the fluid were streaming past it. In the case under consideration the cylinder is moving and the fluid is at rest at infinity; hence the actual path of a particle may be imagined as the path in (1) referred to axes moving with uniform velocity  $u$ . The equation of the path was first obtained by Rankine<sup>1</sup> in the form of a relation between the ordinate  $y$  and the radius of curvature  $\rho$ . It can be deduced from Fig. 1.

We have  $\rho d(2\theta)/dt = \text{velocity of particle at P} = u a^2/r^2$ . By writing down the velocity of P relative to O in a direction at right angles to OP we have

$$r \frac{d\theta}{dt} = u \sin \theta + \frac{u a^2}{r^2} \sin \theta.$$

From these two equations, with  $y$  for  $r \sin \theta$ , we obtain  $2\rho y(1 + a^2/r^2) = a^2$ . But relatively to the cylinder the particle lies on the curve given by equation (1) above; hence, substituting for  $a^2/r^2$  we find the result

$$\frac{1}{\rho} = \frac{4}{a^2}(y - \frac{1}{2}b) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As Rankine pointed out, this represents in general a case of the 'elastic curve'; and, in fact, the path of a particle is one loop of a coiled elastica. We can complete now the solution of (2). For any given particle, fixed by the value of  $b$ , if  $\theta$

<sup>1</sup> W. J. M. Rankine, *Phil. Trans. A.*, vol. 154, p. 369, 1864. The result is erroneously attributed to Maxwell in the article on hydromechanics in the *Encyclopædia Britannica*, 11th ed.

is the angle between the tangent to the path and the axis  $Ox$ , we have on integrating (2)

$$y = \frac{1}{2}b + \left(\frac{1}{4}b^2 + \frac{1}{2}a^2 + \frac{1}{2}a^2 \cos \theta\right)^{\frac{1}{2}} \quad (3)$$

We choose the axis  $Oy$  so that  $x$  is zero when  $y$  is a maximum, and measure the arc  $s$  from this point. Then

$$x = \left(1 - \frac{2}{k^2}\right)s + \frac{a}{k} \operatorname{Eam}\left(\frac{2s}{ka}\right); \quad y = \frac{1}{2}b + \frac{a}{k} \operatorname{dn}\left(\frac{2s}{ka}\right); \quad (4)$$

where the modulus of the elliptic functions is  $k = (1 + b^2/4a^2)^{-\frac{1}{2}}$ .

In terms of elliptic integrals which are usually tabulated, namely  $F(k, \phi)$  and  $E(k, \phi)$  and the corresponding complete integrals  $K$  and  $E$ , we find the following results: the letters refer to the symmetrical curve in fig. 2.

(i) At the point B.  $y = \frac{1}{2}b + a/k$ ;  $\rho = \frac{1}{4}ka$ .

(ii) At C, the widest part of the loop.  $y = \frac{1}{2}b + \frac{a}{k} \sqrt{(1 - k^2)}$ ;

$$x = \frac{1}{2}ka \left\{ \left(1 - \frac{2}{k^2}\right) F(k, 45^\circ) + \frac{2}{k^2} E(k, 45^\circ) \right\};$$

$$\rho = \frac{1}{4}ka / \sqrt{(1 - \frac{1}{2}k^2)}.$$

(iii) At an end point A.  $y = b$ ;  $x = \frac{1}{2}ka \left\{ \left(1 - \frac{2}{k^2}\right) K + \frac{2}{k^2} E \right\}$ ;

$$\rho = a^2/2b.$$

These data are generally sufficient for drawing the curve with considerable accuracy. From the periodicity of the elliptic functions we can also write down the total length of the path ABCD; it is equal to  $kKa$ . As a numerical example, one finds that the total distance covered by a particle initially at a distance  $a$  from the axis, as the cylinder moves from an infinite distance behind to an infinite distance in front of the particle, is approximately  $2a$ ; this is the curve denoted by 1.0 in Fig. 2. It need hardly be pointed out that although the limiting length of path is finite, the time involved becomes infinite.

In Fig. 2, some curves are drawn for various values of the ratio of  $b$  to  $a$ ; except in one case, only half of each complete path is shown. For  $b$  zero, the path is infinite in length and is given by

$$x = a \tanh(2s/a) - s; \quad y = a \operatorname{sech}(2s/a).$$

The cross-marks on the curves indicate the spaces covered in successive equal intervals of time by particles which were simultaneously at similar points (B) of their paths.

2.—With the help of these curves we can trace the changes in any line containing always the same particles. For this purpose we draw the relative stream lines given by (1), for the same values of  $b/a$  as are shown in Fig. 2. We

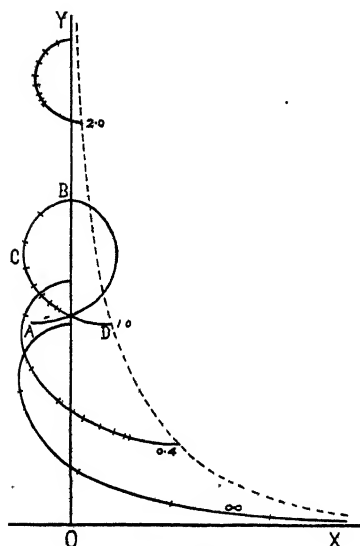


FIGURE 2

superpose this diagram on Fig. 2, with the axes of  $x$  coinciding, and draw a curve through the intersections of corresponding actual and relative paths; displacing one diagram parallel to the direction of motion, we mark again the intersections and obtain the displaced position of the same set of particles. For instance, with the actual paths as in Fig. 2, we obtain by this method the successive positions of a line of particles which at some instant formed a straight line abreast

of the cylinder; these curves are shown for one quadrant in Fig. 3.

The diagram can also be described in another manner. The cylinder moves from left to right. At the instant represented in Fig. 3,  $AB$  is a line of particles abreast of the cylinder; the successive curves to the left are the present positions of particles which were abreast of the cylinder at certain equal intervals of time previously. The unit of time  $T$  is that taken by the cylinder to move through one-quarter of its diameter. Thus the curve  $C^1D^1E^1$  represents the present position of particles which were abreast of the cylinder at  $CDE$  at a time  $5T$  previously. It may be noticed that the circumference of the cylinder forms part

in the limit, of one of the relative stream lines; so that the same particles are always in contact with the cylinder, as the ordinary ideal theory requires.

3.—To trace out the deformation of other lines of particles, it is necessary to adjust first the curves in Fig. 2. For instance, to obtain curves which have been drawn by Maxwell, we arrange the paths in Fig. 3 so that the initial points (A) lie in a straight line perpendicular to  $Ox$ ; then by the same process as before, we obtain the successive forms of a line of particles which lay in a straight line initially

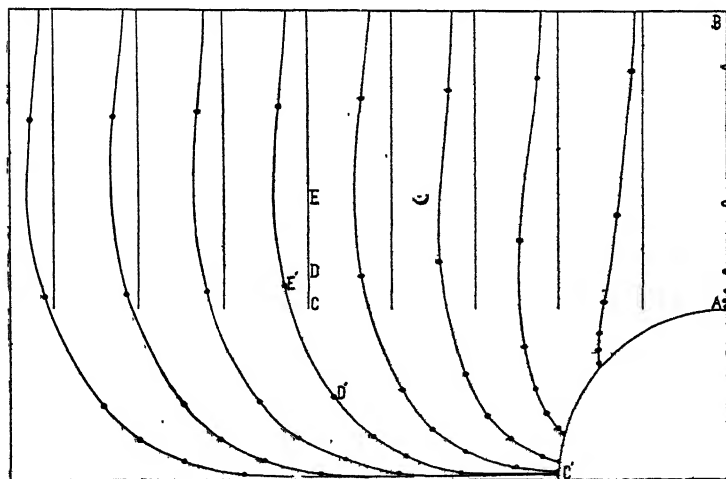


FIGURE 3

when at a great distance in front of the cylinder. We could trace similarly the deformation of groups of particles.

Fig. 4 was obtained by this method; it illustrates the extreme deformation which occurs near the cylinder. Consider for a moment that the cylinder is at rest and the fluid streams past it from left to right. The three enclosed areas, equal in magnitude, are successive positions of the same group of particles.

It has been mentioned already that the ordinary solution of this problem assumes that the fluid is infinitely divisible

into parts retaining the characteristic properties of a fluid. We introduce other limitations when we regard the fluid as made up of a large, but finite, number of particles or molecules which retain their identity during the motion. For such a molecular fluid, it is known that solutions obtained by continuous analysis imply that the molecules move in such a way that their order of arrangement does not alter. Also if we consider a group of molecules forming an element of volume round some point at any time, the same molecules will form an element of volume in the neighbourhood of some other point at any subsequent time; that is, the deformation of an element of volume must be infinitesimal. An inspection of Fig. 4 shows that this condition is not fulfilled in the

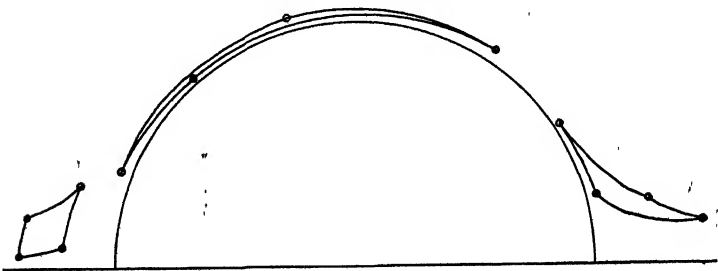


FIGURE 4.

vicinity of the cylinder. One can imagine a curve drawn round the cylinder, not symmetrical fore and aft, within which the conditions are certainly not satisfied. These considerations may help to remove an apparent absurdity. If we examine curves, as Maxwell's, showing the successive forms of lines of particles originally straight in advance of the cylinder, we notice that the cylinder never penetrates through any such line, all of them being looped always round the cylinder. Quite apart from other considerations which enter in the case of an actual fluid, we are relieved from this conclusion by remembering that, on account of molecular constitution alone, there is a region round the cylinder within which the solution obtained by continuous analysis does not represent the true state of motion.

4.—We consider now the paradox to which reference has been made above, returning to the solution of the first two sections. If we imagine the fluid to be contained within a fixed vessel it is clear that, as the cylinder is moved forward, an equal volume of fluid must be displaced backwards. The same argument should hold continuously as we suppose the containing vessel increased indefinitely, and hence in the limit, when we consider motion in an infinite fluid subject to its being at rest at infinity. Thus there should be a permanent displacement of the fluid backwards on the whole. But, according to the paths drawn in Fig. 2, we find that every particle comes to rest ultimately at some point D in advance of its initial position A; so that there appears to be a displacement of the liquid forwards. The interest of this paradox lies partly in its recurrence in various writings. Lanchester<sup>1</sup> states the difficulty and leaves it with the remark: "it is evident that some subtle error must exist in Rankine's argument, the exact nature of which it is difficult to ascertain." Taylor<sup>2</sup> points out how with a finite displacement of the cylinder it can be verified that the fluid is displaced backwards, but with an infinite displacement one has the curious result of a permanent forward displacement. Maxwell<sup>3</sup> raised the same problem many years ago; he admits it as a real difficulty and disposes of it thus: "It appears that the final displacement of every particle is in the forward direction. It follows from this that the condition fulfilled by the fluid at an infinite distance is not that of being contained in a fixed vessel; for in that case there would have been, on the whole, a displacement backwards equal to that of the cylinder forwards. The problem actually solved differs from this only by the application of an infinitely small forward velocity to the infinite mass of fluid such as to generate a finite momentum."

The difficulty arises chiefly from a loose use of the idea of

<sup>1</sup> F. W. Lanchester, *Aerodynamics*, p. 20, 1909.

<sup>2</sup> D. W. Taylor, *Speed and Power of Ships*, p. 10, 1910.

<sup>3</sup> J. C. Maxwell, *Scientific Papers*, vol. ii., p. 210, 1870.

infinity as if it implied a definite state or time, rather than the limiting value of a process which must be defined precisely in each case; unless this is done the problem is really indeterminate. From this point of view, Maxwell's statement seems inadequate, in that it accepts the forward displacement as definitely proved; on the other hand it

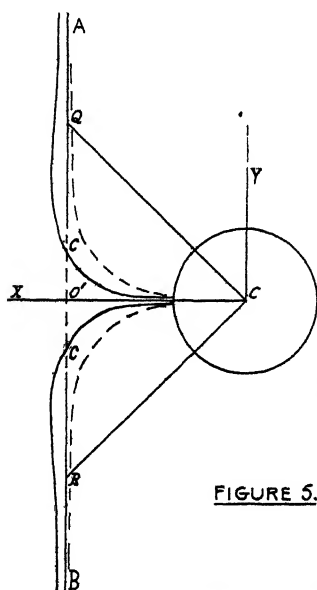


FIGURE 5.

points to a root of the matter, namely, the conditions at infinity. Leaving this till later, we discuss the previous solution as it stands, first stating the possibilities in general terms and then treating them analytically.

In Fig. 5, O is the centre of the cylinder; the curved line represents the particles which were abreast of the cylinder when the centre was at O'. The flow of fluid backwards is given by the difference between the areas behind and in front of the line AO'B. As O'O increases, the points C move outwards along the line AO'B; the dotted curve, which is entirely in front of AO'B, shows the ultimate position of the same particles, according to the paths in Fig. 4, when O'O becomes infinite.

(A) Let  $x, y$  be co-ordinates of any point P on the line AO'B referred to the centre O. If we fix any value of  $y$ , however large, we can make P be within the range O'C by making  $x$  large enough. This is the argument which leads to a permanent forward displacement. It clearly lays more stress on the infinity of extent of liquid fore and aft of the cylinder.

(B) On the other hand, if we fix  $x$ , no matter how large, we can make the point P be beyond C on the line O'A by making  $y$  large enough. By giving more weight to the infinity of liquid abreast of the cylinder, this argument

denies that the limit of the dotted curve in Fig. 5 can ever be attained. These two arguments can, of course, be stated simply in terms of the flow of liquid at any instant across a line behind the cylinder. If we draw lines OQ, OR at  $45^\circ$  to the line OO<sup>1</sup>, then at any time the flow across AO<sup>1</sup>B is forwards in the range QO<sup>1</sup>R and backwards beyond Q and R. According to (A), the range QO<sup>1</sup>R can be made infinite by taking  $x$  large enough; while the argument (B) points to the region within lines at  $45^\circ$  and  $90^\circ$  to the axis OO<sup>1</sup>.

Analytically, the matter reduces to the evaluation of a double integral which gives different values according to the order in which the integrations are performed. We can see this by writing down an expression for the total momentum of the whole liquid in the direction of motion of the cylinder.

Referring to Fig. 1, we have  $ua^2r^{-2}\cos 2\theta$  for the component fluid velocity at any point, or  $ua^2(x^2 - y^2)/(x^2 + y^2)^2$  in terms of rectangular coordinates. Thus with  $s$  for the density of the fluid, the total momentum forward is given by

$$M = ua^2s \iint \frac{x^2 - y^2}{(x^2 + y^2)^2} dx dy,$$

where the integration extends throughout the fluid.

We divide the integration into two parts, writing  $f$  for  $(x^2 - y^2)/(x^2 + y^2)^2$ . First, the region abreast of the cylinder, extending to infinity in both directions, gives without ambiguity

$$M_1 = 4ua^2s \int_0^a dx \int_{\sqrt{a^2 - x^2}}^{\infty} f dy = -\pi sa^2u.$$

For the rest of the fluid, fore and aft of the cylinder, we have

$$M_2 = 4ua^2s \iint f dx dy,$$

where  $r$  ranges from  $a$  to  $\infty$ , and  $y$  from 0 to  $\infty$ .

The integral  $M_2$  has different values according to the order in which the integrations are performed. We have

$$M_2 = 4ua^2s \int_0^{\infty} dy \int_a^{\infty} f dx = 2\pi sa^2u.$$



This evidently corresponds with argument (A) above. Adding  $M_1$  and  $M_2$ , we have a total momentum forwards of  $\pi s a^2 U$  and this agrees with the permanent forward displacement.

On the other hand, we have

$$M_2 = 4ua^2s \int_a^\infty dx \int_0^\infty f dy = 0.$$

This is the argument (B), and it gives a total momentum of  $\pi s a^2 u$  backwards.

We may write the integral  $M_2$  as a limit in the form

$$M_2 = \lim_{b, c \rightarrow \infty} 4ua^2s \int_a^b dx \int_0^c f dy.$$

In this integral with  $b, c$  finite and  $a$  not zero, the order of integration may be inverted without changing the value; we have in either case

$$M_2 = 4ua^2s \lim_{b, c \rightarrow \infty} \left( \tan^{-1} \frac{b}{c} - \tan^{-1} \frac{a}{c} \right).$$

This form brings out the indeterminateness of the problem, for the limit can have any value we please between  $\pi/2$  and 0 according to the limiting value of the ratio  $b/c$ . The argument (A) above supposes that  $b$  and  $c$  are both infinite in such a way that  $b$  is infinitely greater than  $c$ ; while we obtain the result of argument (B) by supposing  $c/b$  infinite in the limit. Another special case would be to suppose  $b$  and  $c$  to become indefinite in a ratio of equality. Then  $M_2$  is  $\pi s a^2 u$  and the total momentum of the fluid is zero. In this case we picture the fluid as of equally infinite extent in and at right angles to the line of motion. Up to the present we have taken the solution of the fluid motion without considering the conditions under which it was obtained. These included the condition that the fluid should be at rest at infinity, that is, the velocity should become infinitesimal as the distance from the cylinder increased indefinitely. If we could imagine the fluid to be contained in a fixed boundary at infinity, the condition to be satisfied there would be the vanishing of the normal component of velocity. At first sight, there would not seem to be much

difference between the two cases, the latter being included in the former. But we have seen that it is necessary to define conditions more precisely in order to avoid ambiguity. We may illustrate this by a definite problem in initial motion for which the solution is known.

Let the fluid be contained within a fixed concentric cylinder of radius  $c$ , and let the inner cylinder be suddenly started with velocity  $u$ . If  $\phi$  is the velocity potential of the initial fluid motion, the boundary condition at the outer cylinder is that  $d\phi/dr$  should be zero. The value of  $\phi$  is

$$\phi = \frac{ua^2}{c^2 - a^2} \left( r + \frac{c^2}{r} \right) \cos \theta.$$

The second part of  $\phi$  represents the fluid motion already studied, with an additional factor  $c^2/(c^2 - a^2)$ . Superposed on this there is a uniform flow backwards of amount  $ua^2/(c^2 - a^2)$ . The total momentum can be found by integrating throughout the liquid as before. In this case there is no ambiguity and it is easily shown that the second term in  $\phi$  contributes nothing to the momentum. Adding the part due to the uniform flow, we find the total fluid momentum to be  $\pi sa^2u$  backwards; this result is independent of the radius of the outer cylinder, and, of course, agrees with elementary considerations.

Now suppose the radius  $c$  to become infinite. The fluid motion then differs from that studied in the previous sections only by a superposed uniform flow backwards of infinitesimal magnitude; but when integrated through the infinite extent of liquid it gives use to a finite momentum  $\pi sa^2u$  backwards. Further, in any finite time the additional term makes no more than an infinitesimal difference to the paths of the particles; but if we attempted to extend the solution to "infinite" time we should be faced with various ambiguities in making any allowance for the extra term.

The velocity potential  $\phi$  for a finite extent of fluid is determinate when the values of  $\phi$  or  $\delta\phi/\delta n$  are given over all the boundaries. If the outer boundary becomes infinite

and  $\phi$  is said to vanish at infinity, the solution is indeterminate by an infinitesimal amount. Consequently the total momentum or flow may be indeterminate to a finite amount. On the other hand, the total kinetic energy of the fluid motion, involving a summation of the square of the velocity, is only indeterminate to an infinitesimal extent.

In conclusion, it appears that the problem is indeterminate unless the infinite boundary of fluid can be defined as the limit of some particular form, and further in that case the conditions satisfied at the boundary must also be considered. At the best the question of what happens in an infinite fluid after an infinite time leads to unreal difficulties; the above discussion may serve to show in what way these arise when we attempt to force to this extent ordinary solutions which give consistent results when treated in a legitimate manner.

## BENZYLORTHOTHIOFORMATE.

By J. A. SMYTHE, D.Sc.

[Read May 11th, 1911.]

During the course of experiments carried out some years ago on the condensation of organic sulphur compounds, the formation of small quantities of a white, crystalline substance, M.P.  $103^{\circ}\text{C}$ ., was observed wherever benzyl mercaptan and hydrogen chloride were brought together in presence of glacial acetic acid. Preliminary analyses showed that this compound resembled the mercaptan in composition; in chemical behaviour, too, there was strong similarity; thus, the compound decolorised iodine like the mercaptan, yielding thereby benzyl disulphide, M.P.  $71^{\circ}\text{C}$ ., and it formed with an alcoholic solution of mercuric chloride an insoluble compound which was decomposed by hydrogen chloride into mercuric chloride and benzyl mercaptan. The molecular weight, determined cryoscopically, was found to be about three times as great as that calculated for the mercaptan.

These facts were suggestive of the view that the unknown compound was a polymer of mercaptan, having the composition  $(\text{C}_6\text{H}_5\text{CH}_2\text{SH})_3$ . Though some doubt existed in the matter until complete analyses had been made and the small and varying yields of the substance accounted for, yet the statement by the author in a recent paper (*Journ. Chem. Soc.*, 1909, 95, p. 350) that "hydrogen chloride has a specific action on benzyl mercaptan," seemed to be well founded. A recent and more thorough examination of the matter than was possible at that time has, however, shown that this statement is erroneous, for the compound has been definitely identified as the benzylester of orthothioformic acid and it has been shown that hydrogen chloride has no action on benzyl mercaptan when dissolved in pure acetic acid. In

the following account, the evidence which has led to the correct understanding of the subject, along with some matters arising out of it, will be detailed:—

ANALYSIS OF THE COMPOUND M.P. 103° C.

0.1060 gram gave 0.2688 CO<sub>2</sub> and 0.0580 H<sub>2</sub>O. C=69.15. H=6.08  
 0.1058 „ „ 0.2678 „ 0.0558 „ C=69.02. H=5.86  
 0.1406 „ „ 0.2583 BaSO<sub>4</sub>. S=25.20.

Molecular weight by freezing point method = 361, 371 364.

Calculated for C<sub>22</sub>H<sub>12</sub>S<sub>3</sub>. C=69.08. H=5.76. S=25.16.

Molecular weight = 382.

A compound of this composition, though with somewhat lower melting point (98° C.), prepared from benzyl mercaptan, caustic soda, and chloroform and behaving towards silver-nitrate like mercaptan itself has been described by M. Dennstedt (*Ber.*, 1878, xi., 2265 and 1880, xiii., 238). The identity of Dennstedt's compound with that under discussion has been proved by direct comparison.

*Synthesis of Dennstedt's Compound.*—(1) 4 c.c. mercaptan, 4 c.c. chloroform, and 30 c.c. caustic soda (5 per cent. solution) were heated for several hours. After distillation in steam to remove unaltered mercaptan and chloroform, the residue yielded on fractionation 1.5 gram of a compound, M.P. 103° C., identical in all respects with Dennstedt's compound<sup>1</sup> and with that prepared by the action of hydrochloric acid on the mercaptan in solution of acetic acid. In addition to some oily matter, 0.5 gram benzyl sulphide was isolated from the products of reaction. The formation of this compound was overlooked by Dennstedt; some interest attaches to the observation as benzyl sulphide is the thioether corresponding to the thio-alcohol or mercaptan and is, doubtless, formed from it by loss of the elements of hydrogen sulphide, thus:—



From the method employed, there can be no doubt that the main product of this reaction, the compound melting at

<sup>1</sup> None of the samples prepared has ever shown the melting point given by Dennstedt.

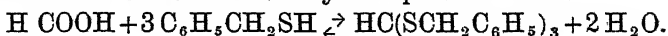
103° C., is, as Dennstedt assumed, the benzyloester of ortho-thioformic acid having the formula  $\text{HC}(\text{SCH}_2\text{C}_6\text{H}_5)_3$ . This will be referred to in the sequel as the thioester. A much more convenient method for its preparation was found in the direct condensation of mercaptan and formic acid.

(2) 5 grams mercaptan (1 mol.) were dissolved in 40 c.c. glacial acetic acid, 4 grams sodium formate (3 mols.) added and the solution saturated with hydrochloric acid gas. After standing overnight, the product was distilled in steam; the residue consisted of 4.2 grams of the pure thioester and the distillate, which smelled strongly of mercaptan, yielded on oxidation with iodine 0.8 gram benzyl disulphide, equivalent to about the same weight of mercaptan.

This method yields a pure product with little labour and is greatly to be preferred to Dennstedt's method. The fact that condensation is not complete, even with excess of formic acid, indicates that the reaction is reversible. This is proved by the following experiment:—

*Hydrolysis of the Thioester.*—1 gram of the thioester was dissolved in 10 c.c. glacial acetic acid and the solution saturated with hydrochloric acid as in the foregoing experiment. On distilling the product in steam the next day, the residue consisted of 0.1 gram unaltered thioester and the distillate took up 0.86 gram iodine (equivalent to 0.84 gram mercaptan) and yielded thereby 0.80 gram benzyl disulphide, M.P. 71°.

It is thus clear that the thioester is hydrolysed into formic acid and mercaptan under the same conditions as lead to its production from these compounds. The reaction is therefore reversible and may be represented thus:—



The extent of hydrolysis proved in the last experiment gives no true measure of the composition at equilibrium owing to the volatility in steam of the formic acid and mercaptan and the continuous resolution of the thioester during the steam-distillation.

*Origin of the Thioester in the Reaction between Hydrochloric Acid and Mercaptan in Solution of Glacial Acetic Acid.*—The ready formation of the thioester (Dennstedt's compound) from formic acid and mercaptan having been established, it seemed likely that this reaction would account for the production of the thioester when hydrogen chloride, acetic acid, and benzyl mercaptan were brought together. Assuming this to be the case, the question arose, whence came the formic acid? The mercaptan was prepared by the action of benzyl chloride on an alcoholic solution of sodium sulph-hydrate, the product being distilled in steam, the mercaptan shaken out of the distillate with chloroform and purified by distillation under reduced pressure. The formic acid (or some derivative reacting similarly with mercaptan) might thus have come from the alcohol used to dissolve the sulph-hydrate, especially as rectified methylated spirit had occasionally been used; or it might have its origin in the chloroform employed in the extraction of the mercaptan; or, finally, it might have been present in the glacial acetic acid used as solvent for the mercaptan.

Parallel experiments, using the same quantity of mercaptan and acetic acid, but adding in one case 20 c.c. methylated spirit, proved that impurity in the spirit had no influence on the reaction, for the weight of the thioester produced in each case was the same. The second possibility was ruled out by the observation that in chloroform solution (and the same applies to carbon tetrachloride) hydrogen chloride has no action at all on mercaptan. There remained thus only the acetic acid as a likely source of the formic acid. At this stage, the author's attention was drawn to a statement (*Journ. Soc. Chem. Ind.*, No. 2, Vol. xxx., Jan. 31, 1911, p. 82) that commercial glacial acetic acid commonly contains formic acid, in quantity up to 0·8 per cent. In the same communication a convenient method for the estimation of the formic acid, based on the reduction of mercuric chloride, is given.

To test the question at issue, a quantity of commercial glacial acetic acid, nearly one litre, was fractionated by freezing and liquation and divided thus into three parts: A, 300 c.c., the purest; B, 380 c.c., the middlings; and C, 285 c.c., the impure mother-liquors. In each of these fractions, the quantity of formic acid was determined by reduction of mercuric chloride (*op. cit.*). The results are as follows:—

Sample A contained 0.078 gram formic acid, *i.e.*, 0.026 gram per 100 cc.

"	B	"	0.319	}	"	"	0.085	"	"	(mean value)
			0.324							
"	C	"	0.655	}	"	"	0.230	"	"	"
			0.658							

50 c.c. of sample A and 3 c.c. of mercaptan gave, after saturation with hydrogen chloride, only a trace of the thioester. 50 c.c. of sample C, however, and 3 c.c. of mercaptan gave, on saturation with hydrogen chloride, a copious crystalline precipitate after keeping some days. The liquid was decanted from the crystals and a further slight amount of crystalline matter obtained by cooling with ice and addition of water until the liquid became slightly turbid. The crystalline compound obtained in this way proved to be the pure thioester, M.P. 103° C. The weight of the combined crops was 0.95 gram, equivalent to 0.114 gram formic acid or 0.228 gram formic acid per 100 c.c. of the sample—a result in excellent agreement with the determination made by the mercuric chloride method.

The production of the thioester might thus be used for the quantitative determination of formic acid in glacial acetic acid; for obvious reasons, however, it is not likely to supplant the method based on the reduction of mercuric chloride. It may be noted in passing that, though the reaction leading to the formation of the thioester is reversible, the sparing solubility of this compound in cold, glacial acetic acid allows of its practically complete separation from solution, and further, that, according to the law of mass action, the reaction is very sensitive to excess of mercaptan. Thus, when these two conditions are observed, *viz.*, excess of



mercaptan and ice-cold temperature, one may expect that the formic acid will be, within practical limits, completely precipitated as the ester of orthothioformic acid.

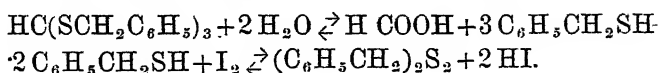
It is clear from the foregoing experiments (1) that hydrochloric acid has no specific action on benzyl mercaptan, (2) that the crystalline compound, M.P.  $103^{\circ}\text{C}$ ., produced when these two substances are brought in contact with commercial glacial acetic acid is identical with the benzyl orthothioformate of Dennstedt, and (3) that this compound owes its formation to condensation of the mercaptan with formic acid, present as impurity in the acetic acid. The last point is confirmed (if confirmation is necessary) by reference to the accounts of older experiments, from which it is seen that the yield of the thioester is proportional to the quantity of acetic acid used, the mercaptan being always in excess. The data in four cases are as follows:—

	Glacial Acetic Acid Taken. CC.	Yield of Thioester. Grams.	Grams of Formic Acid per 100 cc. Acetic Acid Calculated from the Yield of Thioester.
(1)	60	3.4	0.67
(2)	50	3.3	0.79
(3)	30	1.4	0.59
(4)	20	1.1	0.66

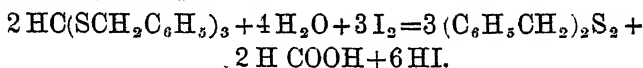
No record of the samples of acetic acid used in these experiments has been kept; it would appear that the acid at present obtainable is much purer, containing only about 1 part per 1,000 of formic acid.

*Action of Iodine on the Thioester.*—It has been stated already that iodine reacts with the thioester, as it does with benzyl mercaptan, producing benzyl disulphide. The first attempts to utilise this reaction for estimating the thioester led to discordant results, the explanation of which appeared to lie in the reversibility of the processes involved. To account for the formation of benzyl disulphide, it is natural to assume that the thioester is first hydrolysed and that the mercaptan thus formed is oxidised by the iodine to the disulphide. The first of these reactions has been proved to be reversible and the second can be readily shown, by direct

experiment, to be reversible also. The reaction thus takes place in two stages, each of which is reversible:



Many efforts, in which the author has had the assistance of Mr. A. Jaques, have been made to determine the state of equilibrium of these combined actions, but without success; similarly, attempts to synthesise the thioester from benzyl disulphide, formic acid and hydriodic acid have failed, and the reason would seem to be that, under the conditions of experiment, the second reaction is practically complete, *i.e.*, the oxidation of the mercaptan by iodine is not restricted by the reduction of the disulphide by hydriodic acid. It has, in fact, been found possible to estimate the thioester accurately by means of standard iodine solution, the reaction being, in certain circumstances, practically complete and expressed by the equation:—



The following experiments give the details of these estimations, and they show also in a rough manner the accelerating influence of temperature and a catalyst (hydrochloric acid) on the speed of the reaction. For the purpose of the experiments, a standard solution of the thioester containing 1 gram in 250 c.c. of alcohol (about 98 per cent.) was made at 50° C.; 25 c.c. of this solution were used in each case. The standard iodine solution (in potassium iodide) contained 0.01142 gram iodine per c.c.; a solution of sodium thiosulphate of corresponding strength was used for determining the excess of iodine, and the hydrochloric acid employed as catalyst was the ordinary, pure concentrated acid. If the reaction takes place according to the above equation, it follows that 25 c.c. of the thioester solution will take up 8.75 c.c. of the iodine solution.

(1) 25 c.c. of the solution cooled to 16° C. and one drop of

iodine solution added. The colour persisted for  $1\frac{1}{2}$  hours. Second drop of iodine solution took about the same time to disappear.

(2) 25 c.c. heated  $\frac{1}{2}$  hour after addition of 10 drops of hydrochloric acid and the solution cooled to  $16^{\circ}\text{C}$ . The smell of mercaptan was noticeable and the solution immediately decolorised 1 c.c. of iodine solution.

(3) 25 c.c. kept at a temperature of  $40^{\circ}\text{C}$ . and iodine solution added one drop at a time. The time taken to decolorise each drop was noted, with the following results: 4 successive drops took 5, 5, 5, and  $5\frac{1}{2}$  minutes, respectively, for decolorisation. 5 drops of hydrochloric acid were now added; 2 drops of iodine took 3 and 4 minutes for decolorisation. After addition of 15 drops more of hydrochloric acid, 4 drops of iodine took  $1\frac{1}{2}$  minutes each for decolorisation, and after a further addition of 20 drops of hydrochloric acid, each of 12 drops of iodine was decolorised in about 20 seconds.

(4) 25 c.c. heated to  $75^{\circ}\text{C}$ . The first ten drops of iodine were decolorised in 1 minute, the next ten drops in  $\frac{3}{4}$  minute. After addition of 10 drops of hydrochloric acid, 10 drops of iodine were decolorised in 5 seconds. This reaction was carried to completion and the volume of iodene solution used was found to be 8.80 c.c.

The next three determinations were made under comparable conditions, the only difference being in the amount of catalyst present.

	Volume of Thioester Solution. CC.	Tempera- ture. Degree C	HCl Added.	Time taken to Complete Reaction. Mins.	Volume of Standard Iodine Used. CC.
(5)	25	75	None	40	8.75
(6)	25	75	5 drops	20	8.75
(7)	25	75	15 drops	10	8.80

From experiments 4, 5, 6, and 7, it follows that the gram molecule of the thioester is almost exactly equivalent to three gram atoms of iodine [ $\text{HC}(\text{SCH}_2\text{C}_6\text{H}_5)_3 = 3\text{I}$ ], or, in other words, that the reaction between the two substances in dilute alcoholic solution is practically complete. When experiment

1 is compared with the rest, it seems obvious that the reaction between iodine and the thioester takes place in two stages, the first consisting in the hydrolysis of the ester, the second in the oxidation of the mercaptan. The velocity of hydrolysis increases greatly with the temperature when water is the catalyst (*see* experiments 1, 3, and 4) and with the amount of the catalyst (hydrochloric acid) at constant temperature (experiments 3 and 4). The catalytic influence of the hydriodic acid formed in the reaction would seem to be very slight. The velocity of reaction in the second stage, *i.e.*, oxidation of the mercaptan, is probably so great as to be beyond measurement.

## THE RELATIONSHIP BETWEEN THE CHEMICAL COM- POSITION AND THE POSITION OF SOME NORTH COUNTRY CLAYS.

By A. A. HALL, M.Sc., Ph.D.

[Read May 11th, 1911.]

Although many analyses of fire-clays have been made and published, analysts in the past have given little attention to the position of the clays analysed, and have directed their attention chiefly to those constituents present in large quantities to the neglect of those compounds which are only present in small percentages. The object of the present series of analyses was to see whether the clays themselves were affected in composition by the strata above them, more particularly whether those fire-clays found under coal differed in any essential way from those clays found under limestone or sandstone; also whether the clays directly in contact with the coal differed from those found at a greater distance from the coal floor, and at the same time find out whether these underclays may be truly looked upon as exhausted soils.

In order to determine these various points it was

essential that complete analyses should be made as accurately as possible. Five different clays were analysed, two lying under limestone, one under sandstone and two under coal. From one of the latter several samples were taken at varying depths.

TABLE I.

	1	2	3	4	5	6	7	8	9
Moisture (loss at 110 C)	1.97	1.60	1.80	3.60	}87.00	2.10	2.00	2.10	2.20
Organic matter and water	6.00	10.60	5.30	14.30		9.40	8.10	8.00	7.75
SiO <sub>2</sub> ...	63.69	55.44	65.55	42.70	6.53	54.26	56.00	56.10	56.20
Al <sub>2</sub> O <sub>3</sub> ...	23.01	25.31	21.21	32.95	3.66	29.02	29.08	29.28	29.25
MnO ...	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Fe <sub>2</sub> O <sub>3</sub> ...	2.40	2.30	2.00	2.46	1.172	1.80	1.70	1.80	1.70
P <sub>2</sub> O <sub>5</sub> ...	0.034	0.037	0.03	0.27	0.055	0.05	0.028	0.025	0.025
TiO <sub>2</sub> ...	1.18	1.23	1.21	0.98	0.13	1.14	1.17	1.14	1.15
CaO ...	.65	0.62	0.50	0.54	0.78	0.75	0.88	0.80	0.75
MgO ...	—	0.50	0.00	0.24	0.45	0.08	0.08	0.10	0.09
K <sub>2</sub> O ...	1.08	1.80	1.50	1.33	0.17	1.29	1.08	1.00	1.01
Na <sub>2</sub> O ...	0.25	0.40	0.98	0.40	0.053	0.20	0.15	0.09	0.10
CO <sub>2</sub> ...	—	—	—	—	—	—	—	—	—
	100.264	99.837	100.08	99.77	100.00	100.09	100.268	100.435	100.225

Figures in Table II., with the exception of analysis 5, were calculated from those of Table I., and give the composition of the ignited clays. Analysis No. 5, Table II., gives the amounts found by actual analysis, those in Table I. being calculated from them.

TABLE II.

	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub> ...	69.03	63.26	70.53	52.15	50.00	61.30	62.10	62.11	62.26
Al <sub>2</sub> O <sub>3</sub> ...	24.88	28.88	22.83	40.26	28.10	32.74	32.20	32.41	32.40
Fe <sub>2</sub> O <sub>3</sub> ...	2.62	2.63	2.15	3.01	9.01	2.043	1.87	1.99	1.883
P <sub>2</sub> O <sub>5</sub> ...	0.037	0.042	0.03	0.33	0.42	0.057	0.03	0.028	0.027
TiO <sub>2</sub> ...	1.283	1.407	1.31	1.21	1.00	1.29	1.29	1.262	1.27
CaO ...	0.70	0.71	0.54	0.66	6.00	0.85	1.08	0.88	0.83
MgO ...	0.00	0.57	0.00	0.28	3.50	0.08	0.08	0.11	0.10
K <sub>2</sub> O ...	1.18	2.05	1.61	1.62	1.30	1.42	1.19	1.11	1.12
Na <sub>2</sub> O ...	0.27	0.451	1.00	0.48	0.40	0.22	0.16	0.10	0.11
	100.00	100.00	100.00	100.00	99.73	100.00	100.00	100.00	100.00

Nos. 1 and 2 were both Corbridge fire-clays, found under limestone.

No. 3 was found under sandstone at High Shield, Hexham.

No. 4 came from the Victoria Garesfield Colliery, and was found under coal.

Nos. 5-9 were found under coal at the Lambton Collieries.

Clays Nos. 1 and 2 were both Corbridge pottery clays found under limestone of lower carboniferous age, 1 being a sample from Messrs. Jameson's main seam under Gallows Hill, Corbridge.

These clays were similar in appearance, both being fine grained clays grey in colour.

Clay No. 3 was a sample from High Shield, Hexham, and was found under sandstone of millstone grit age. This clay was light in colour and from its appearance it was obvious that it contained some free silica.

Clay No. 4 was a sample from the Victoria Garesfield Colliery, Co. Durham, and was found under coal upper carboniferous, it contained many fossils, was dark in colour, fine grained and soapy to the touch.

Clays Nos. 5 to 9 were all samples taken from the Lambton Collieries' main seam and represent three feet of clay at varying depths, No. 5 being nearest to the coal floor. All these clays were dark in colour, fossiliferous and soapy to the touch.

For the analytical methods used I am indebted largely to "The Analysis of Silicate and Carbonate Rocks" by W. F. Hildebrand.<sup>1</sup>

The clay was brought into solution by fusion with sodium and potassium carbonates and extraction with hydrochloric acid.

The true silica content was determined by evaporating the silica obtained in the usual way with hydrofluoric and sulphuric acids, the small residue was added to the iron, alumina and titania precipitate. This precipitate after weighing was fused with about seven times its weight of sodium pyrosulphate for about half an hour and then dissolved in dilute sulphuric acid. The iron was estimated by reduction with hydrogen sulphide and subsequent titration with standard potassium permanganate. The titanium was then estimated by the colorimetric method using hydrogen peroxide. It was found that the small quantity

<sup>1</sup> *United States Geological Survey, Bulletin 305 Series E.*

of iron present in these clays had no appreciable effect upon this determination. The lime, magnesia and phosphorus were determined by the usual methods and the alkalies by the method of J. Lawrence Smith.<sup>2</sup>

These analyses show that the strata immediately above the clay has little or no influence upon its composition at any distance from the junction of the two. It is surprising that the clay found under limestone has not a greater percentage of lime than that found under sandstone or under coal, also that none of the clays analysed, whether found under carbonate rocks or not, contained any carbonate.

This impermeability of the clay to outside influences or leaching from outlying rocks is further brought out by analysis No. 5, Table II., which is a sample of clay taken from the junction of the clay and the coal. From this analysis it seems as if substances which had been able to permeate quite easily through the mass of the coal had been immediately stopped on coming in contact with the clay. The element which shows this most clearly is the phosphorus. The percentage of phosphorus pentoxide in this sample (5) is nearly eight times as great as in the clay a few inches beneath and more than ten times as great as in the clay a foot deeper; in this connection it is interesting to note that experiments carried out at Rothamstead have shown that after placing soluble phosphates upon the soil for forty years it was found that no appreciable quantity had sunk more than an inch below the depth of soil turned over by the plough.<sup>3</sup>

The great difference which exists between the ash of the coal and the clay directly beneath it is clearly shown by some analyses by E. Riley of the Coal Ashes and Clays of the Dowlais Coalfield of South Wales.<sup>4</sup>

Table III. gives the average composition of eight of his underclays and of four of his coal ashes calculated on the ignited clay or ash.

<sup>2</sup> *Annalen Chem. und Pharm.*, vol. 159, 1871, p. 82.

<sup>3</sup> *The Chemistry of the Farm*, by R. Warrington, page 70.

<sup>4</sup> Percy's *Metallurgy*, pages 98 and 352.

TABLE III.

			Clay.		Ash of Coals.
SiO <sub>2</sub>	...	...	60·16	..	34·30
Al <sub>2</sub> O <sub>3</sub>	...	...	32·57	...	34·90
Fe <sub>2</sub> O <sub>3</sub>	...	...	3·30	...	15·94
P <sub>2</sub> O <sub>5</sub>	...	...	—	...	1·67
CaO	...	...	0·42	...	4·12
MgO	...	...	1·18	...	4·42
K <sub>2</sub> O	...	...	2·37	...	1·38
SO <sub>2</sub>	...	...	—	...	3·27
			100·00		100·00

These figures show similar differences between the ash of the Dowlais coals and of the clays under them, as analyses 5 and 6 of Table II., namely, increase in the silica content of the clay and considerable diminutions in the iron, phosphorus, calcium, and magnesium. This average constitution of Riley's eight clays found under coal is remarkably similar to the analyses in Table II. of those clays found under coal, namely, 4 to 9. This is perhaps not so surprising when we consider that although these clays are found widely apart they have probably been formed from similar materials under similar conditions.

Unfortunately, Riley did not estimate the phosphorus in his clays, but the analyses of Table II. show that these clays as they are to-day, in comparison with ordinary soils, whose minimum phosphorus content is about 0·06 per cent., are very poor, almost exhausted soils.

In order to further demonstrate this fact, a mixture of clover and barley seeds were sown in clays Nos. 4 and 9 and also on filter paper, the phosphorus content in each experiment being, respectively 0·27, 0·025, and 0·00, and these three experiments were kept under identical conditions of light and moisture. After two weeks the growth in Experiment 1 was stronger and of better colour than in 2 or 3. After five weeks Experiment No. 1 had a strong growth, No. 2 had practically stopped growing, whilst No. 3 had begun to wither.



The general tendency seems, from these analyses for the clays found under coal, to be poorer in silica and richer in alumina than those found under limestone or sandstone, the iron remains fairly constant except in those clays which are evidently closely in contact with the coal.

The titanium, probably present as rutile<sup>5</sup> in the clays, is remarkably constant, the two extreme values found in these five clays being 1.21 per cent. and 1.407 per cent.

In 1862 E. Riley<sup>6</sup> remarked upon the occurrence of titanium in clays. He found titanium in every fire-clay or brick which he examined, the percentages varying from 0.42 to 1.05 per cent. Since then many observers have noticed its occurrence, usually the amount found has been about 1 per cent. In those analyses of clays in which the titanium has not been estimated it is probable that it has been included with the alumina.

The importance of the estimation of the titanium and the effect of even small quantities of it upon the refractoriness of the clay has been shown by Messrs. Seger and Cramer, of Berlin,<sup>7</sup> and more recently by Ries,<sup>8</sup> who showed that even one half per cent. of titania lowered the fusing point of the clay half a seger cone.

The percentages of potash and soda present are, as one would expect in good fire-clays, low; whether in the case of the clays under coal this is due to the removal of alkalies by the plants growing upon it in the coal age or not is difficult to say; it seems, however, as if the clays found under coal were more likely to be good fire-clays, *i.e.*, be low in alkali content, than those which have never been in contact with coal. It may be that beds of fire-clay with limestone or sandstone roofs once had coal (or at least vegetation) above them and that this was denuded off before the deposition of the limestone or sand, but it is unlikely that all fire-clays

<sup>5</sup> W. M. Hutchings, *Geol. Magazine*, 1890, p. 264.

<sup>6</sup> *Quart. Journ. Chem. Soc.*, 1862, xv., p. 311.

<sup>7</sup> Seger's Collected Writings, I., p. 519.

<sup>8</sup> *N. J. Geol. Surv. Fin. Rept.*, VI., p. 71, 1904.

thus situated were once beneath coal. With regard to the question as to how the composition of the clays varied with the depth, the analyses 5, 6, etc., show that after a very short distance the composition became constant and remained so.

In conclusion, I must thank Messrs. Neilson and Jameson for the specimens of clay with which I have worked, and Professor Lebour for help and advice during the course of the investigation.

## BOULDERS COMMITTEE.

### REPORT NO. 5. MAY, 1911.

The following boulders and pebbles have been collected or determined by members of this Committee since the last report was issued:—

1. Collected by S. R. HASELHURST—

Percy Square to Spanish Battery, Tynemouth.

Basalt, amygdaloidal with large crystals of Anorthite; Volcanic series of Borrowdale; Red sandstone; Syenite; Porphyrite (St. Abbs Head); Micaceous sandstone.

2. Collected by E. MERRICK—

(a) Cowpen Brick Works (late Standard B.W.)

Red fossiliferous Carboniferous Limestone; Syenite; Andesite; Porphyrite; Three boulders of chalk.

(b) Sand Pit, South View, Ryton.

Red granite; Volcanic series of Borrowdale; Ferruginous grit; Threlkeld granite.

(c) Bricks, Limited, Forest Hall.

Red porphyrite.

3. Collected by Dr. WOOLACOTT and E. MERRICK—

From foundations of new buildings for Art department, Armstrong College.

Carboniferous Limestone; Whin Sill; Volcanic series of Borrowdale; rhyolite, 1 cubic foot; Grey granite (Dalbeattie); Sandstone.

4. Collected by Dr. WOOLACOTT and G. T. MACKAY—

A boulder of decomposed Laurvik Syenite or similar rock from Christiania Fiord was observed on the coast about a mile north of Castle Eden.

## 5. Collected by A. BALL—

A piece of Laurvik Syenite from Christiania was collected from the foundations of bridge across Castle Eden Dene.

(Note.—The two latter boulders, probably of Scandinavian origin, are of great interest, as being the most northerly recorded occurrence of Scandinavian rocks in the English drift.)

## 6. Collected in Northumberland by DR. SMYTHE—

- (a) Pebble Bed. Horsebridge Head, near Newbiggin. Result of many years' collecting.

*Sedimentary.* Sandstone, commonest constituent, often containing plant remains (*Lepidodendron*, *Calamites*); Magnesian Limestone abundant (one specimen with *Fenestella retiformis*); Carboniferous Limestone, not common; fossils often occur *Productus*, *Lithostrotion*; Greywacke, not common; Chalk flints; Chalk, 1; Cherts and jaspers, 22.

*Igneous and metamorphic.* Whinstone, fairly common, pebbles up to 1'; of 210 other rocks there were 30 granites, white, grey, red, up to 6"; 20 mica and hornblende schists up to 8"; 56 porphyrites (many certainly from Cheviots); 3 glossy porphyrites and 4 andesites (Cheviots); 15 quartz porphyries with white, pink, green and red groundmass, up to 6"; 17 syenites; 3 mica porphyrites; 1 diorite; 61 weathered rocks, mostly porphyritic.

- (b) Akenshaw Burn.

Black chert abundant. Granite (grey and red), 10; Syenite, 3. Diorite. Porphyrite. Amygdaloidal basalt.

- (c) Whickhope Burn.

Black chert, abundant. Granite, 4; Quartz porphyry, 2.

- (d) Chirdon Burn.

Granites, 8; Syenite; Greywacke; Basalt.

- (e) Pundershaw Burn.

Granites, 7; Carboniferous Limestones crowded with spines of *Productus*; Porphyrites, 2; Volcanic series of Borrowdale (?); Quartz porphyry. Syenite.

- (f) Coldcoates, Wark's Burn.

Red sandstone (Permian or Trias). Granites, 11. Mica syenite, 1. Volcanic series of Borrowdale, 1.

- (g) Coal Cleugh. Middle Burn. Wark's Burn.

Syenite (same rock found in Pundershaw and Sweethope drift); Granites, 7; Quartz porphyrites, 3; Syenite; Porphyry; Greywacke; Diorite.

- (h) Deposit foot of Lyne Burn.

Flints, 5; Chalk; Garnetiferous mica schist (Pitlochrie?), 4; Magnesian Limestone abundant, fossiliferous; Mica Schist, 2;

Basalts (abundant); Quartz porphyry; Syenite; Cheviot porphyrites, 16; Trachyte; Chert, 2; several greywackes; Limestone and sandstone.

(*Note*.—Whickhope and Akenshaw drift dam the Wansbeck at Mitford.)

Volcanic series of Borrowdale occur south of Wark's Burn (present in Liddle Hall Kaims).

Striations have been observed on the rock surface by Dr. Smythe at the following places:—

Barrow Hill (Alwinton), 800' E.

Harbottle Hill (Alwinton), 950' E. by N.

Amerside Law (Chillingham), 1,000' S. by W.

Bellshill, S. 20° E.

All these striations were on sandstone.

#### NOTE ON A BURIED ESCARPMENT.

The existence of a preglacial escarpment buried by drift has been disclosed recently in a clay garth about 100 yards east of Clousden (or Closing) Hill, Forest Hall. At the south end of the workings a rocky scarp, striking E. and W. and evidently a continuation of the bed which comes to the surface at Clousden Hill, is exposed. The edge of this scarp is highly glaciated, the direction of the striæ being N.W.-S.E. The total depth of boulder clay proved close to the scarp-face is about 40 feet and as the top of the escarpment is only about 10 feet below the surface level, the height of the escarpment must have been at least 30 feet. It is probable, however, that it was considerably more.

J. A. S.

PAPERS READ BEFORE THE SOCIETY, SESSION 1910-1911.

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GENERAL MEETINGS.

NOVEMBER 24TH, 1910.

"The Wanderings of a Geologist in the Shan States,"\*  
by J. Coggin Brown, B.Sc.

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JANUARY 20TH, 1911.

"Then and Now," by Professor Bedson.

Dr. Bedson gave an account of the development of the atomic theory of matter. He pointed out that exactly a hundred years ago Avogadro enunciated the hypothesis which is associated with his name.

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MAY 11TH, 1911.

"The Present Position of Wireless Telegraphy," by  
Professor Stroud.

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SECTION A.

DECEMBER 1ST, 1910.

"The Detection of Harmonics in an Alternating Current," by H. Smith, B.Sc.

Mr. Smith explained that, as a pendulum can pick up the vibration of another pendulum by resonance, or a tuning fork commence to vibrate under the influence of another similar tuning fork, so in alternating currents: the harmonics of one circuit can produce corresponding harmonics in another, which can be detected by means of a telephone.

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FEBRUARY 2ND, 1911.

"The Relationship between the Percentage Amount of Fat in Milk and the Times of Milking,"\* by S. H. Collins, M.Sc.

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FEBRUARY 16TH, 1911.

"Some Notes on Point Discharge," by Professor Thornton.

"The Spectrum of the Paulsen Arc," by Miss O'Connor, B.Sc.

Miss O'Connor showed that in the case of the oscillating arc the spectrum is almost entirely that of the atmosphere, while the non-oscillating arc shows the line spectrum of copper.

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MAY 18TH, 1911.

"The Relationship between the Chemical Composition and the Position of some North Country Clays,"\* by A. A. Hall, Ph.D.

"The Occurrence and Determination of Formic Acid in Commercial Glacial Acetic Acid,"\* by J. A. Smythe, D.Sc.

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## SECTION B.

DECEMBER 6TH, 1910.

"Some Chemical and Structural Features of the Magnesian Limestone of Durham," by D. Woolacott, D.Sc.

"Some Features of the Permian of Northumberland,"\* by S. Rennie Haselhurst, B.Sc.

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DECEMBER 13TH, 1910.

"Note on the Formation of Kaolinite in Coal Measure Shales,"\* by R. C. Burton, B.Sc.

"Note on a Buried Escarpment,"\* by J. A. Smythe, D.Sc.

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JANUARY 24TH, 1911.

"The Animal Remains of *Corstopitum*," by Professor Meek and R. A. H. Gray, M.A.

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FEBRUARY 21ST, 1911.

"The Morphogenesis of Bone," by A. D. Peacock, B.Sc.

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MARCH 14TH, 1911.

"The Geology of the South-west of France," by E. G. Clarke, B.Sc.

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MAY 30TH, 1911.

"Note on the Process of Reproduction in the Lichen Peltigera," by O. V. Darbishire, Ph.D.

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## SECTION C.

DECEMBER 15TH, 1910.

"Clebsch's Representation of Quartic-surfaces having a Nodal Conic," by Professor C. M. Jessop.

"Some Notes on Determinants," by Professor P. J. Heawood.

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MARCH 10TH, 1911.

"Orbital Motion in a Resisting Medium," by Mr. G. R. Goldsborough.

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## SECTION D.

DECEMBER 2ND, 1910.

"Heraldry," by Mr. C. H. Blair.

---

FEBRUARY 24TH, 1911.

"Medals Illustrative of English History," by Mr. Philip Spence.

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## SECTION E.

DECEMBER 8TH, 1910.

"A New Steam Trap,"\* by Mr. E. M. Eden.

---

JANUARY 20TH, 1911.

"Brush Resistance," by Professor Thornton.

"The Interaction of Air-pump and Condenser,"\* by J. Morrow, D.Eng.

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FEBRUARY 9TH, 1911.

"The History of the Mutual Development of Metallurgy and Engineering,"\* by Professor Louis.

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MARCH 3RD, 1911.

"The Displacement of the Particles in a Case of Fluid Motion,"\* by T. H. Havelock, D.Sc.

"A Note on a Geometrical Problem," by J. T. Dixon.

Mr. Dixon showed how to solve the problem of drawing a tangent to to any hyperbola from an external point.

Papers marked (\*) have been published in the *Proceedings*.



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### THE RATE OF EVOLUTION OF HYDROCYANIC ACID FROM LINSEED UNDER DIGESTIVE CONDITIONS.

By S. H. COLLINS.

[Read December 11th, 1911.]

In the *Journal of the Society of Chemical Industry*, 1908, page 432, Henry and Auld state, "If further investigation proves that the generally innocuous character of linseed cake is due to the fact that the glucosidolytic enzyme originally present in the seeds is rendered inactive in the hot process of expressing the oil."

The following investigations show that the generally innocuous character of both linseed and linseed cake must often be due to other causes.

Among the important conditions under which linseed must be digested, neither temperature nor removal of end products can be neglected. For this purpose I have digested linseed at temperatures approaching those of animal life and have removed the hydrocyanic acid and other volatile products by a stream of inert gas. In Fig. 1 the inert gas enters at N, bubbles through the evaporator V, passes through the rubber connection C to the absorber B, through E to meter M, passing out by exit X. W is a water bath, heated by gas controlled by thermometer and thermostat, not shown in the diagram. The thermostat described on page 110 proved particularly suitable for this purpose. For most of the work here described, hydrogen was used as the inert gas, the hydrogen generator and purifier described on page 107 working more satisfactorily than any other form tried.

A regular flow of gas through such an apparatus is quite impossible without some kind of gas governor. The gas governor used in the coal-gas testing apparatus prescribed by the gas referees was used in the early work, but proved too cumbersome, and was replaced by the governor and tap described on page 110. The exit X from the meter in Fig. 1 is attached by rubber tube to the entry N of the governor in Fig. 5. The working pressure, that is the height GH in Fig. 5, is about  $1\frac{1}{2}$  cm. for hydrogen, and about 3 cm. for air; the tap A in Fig. 5 is nearly shut

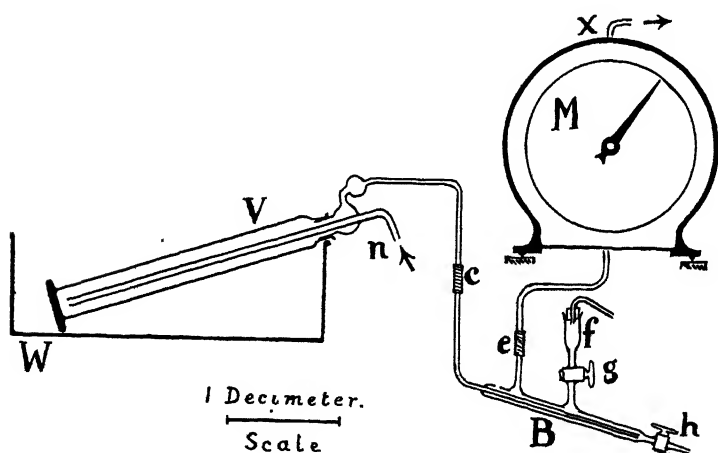


FIGURE 1.

for hydrogen and half open for air, the different specific gravities of the two gases accounting for the different adjustments.

To carry out an experiment with the apparatus, one gramme of linseed and 50 cc. water are placed in the evaporator V, 5 cc. sodium hydrate of about one-thirtieth normal strength are passed through the tap G into the absorber B, and the current of gas started. On starting, clock, meter and thermometer are all read. From time to time the sodium hydrate solution in B is removed by tap H and a fresh supply of sodium hydrate added through G.

As B is under slight pressure during experiment, the liquid has to be forced in by gently blowing through the tube F. By these means any hydrocyanic acid in the vessel V is evaporated by the current of gas and absorbed in B and obtained in several fractions in small test tubes marked at 5 cc. To each of these test tubes is added one drop of a solution of ferrous sulphate (12 per cent.), shaken up and allowed to stand for one hour, after which one drop of dilute sulphuric acid (1:2) is added, the tube again shaken and allowed to stand for at least 36 hours. The colours are matched with standards made from a solution of potassium

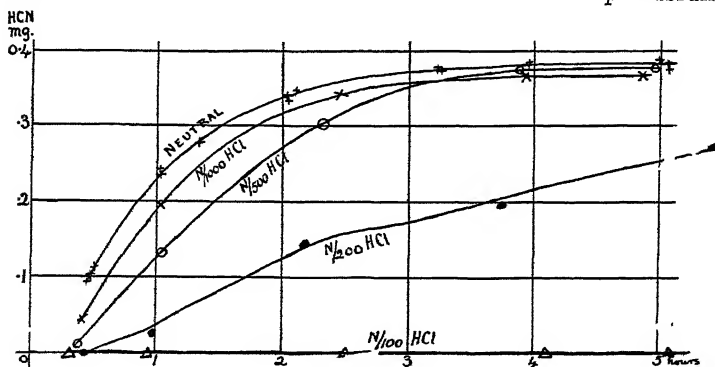


FIGURE 2.

cyanide,<sup>1</sup> with iron and acid in exactly the same way. The potassium cyanide solutions<sup>1</sup> are verified by one-hundredth normal silver nitrate. Whilst potassium cyanide solutions keep very badly, the standards of prussian blue keep remarkably well. Tubes twelve months old, stoppered with waxed corks, when compared with tubes four days old, only showed a 2 per cent. variation. A set of standards from 0.01 mgm. to 0.30 mgm. have proved most useful. Tubes were usually read when three, four and five days old and the mean of the three readings taken as correct. The third place of decimals is only obtained by visual interpolation.

<sup>1</sup> As commercial Potassium Cyanide is very impure it is preferable to distil hydrocyanic acid into potassium hydrate solution to make stock solutions.

When linseed and water are treated by this method, one particular sample of Calcutta linseed yielded 0.380 milligrammes of HCN per gramme of linseed, with a probable error of  $\pm 0.004$  for one experiment. The velocity of reaction (Curve, Fig. 2) was such that one-half of the total amount was yielded in 46 minutes,<sup>2</sup> whereas hydrocyanic acid from KCN + (10 to 50) HCl yielded one-half the total amount in 26 minutes,<sup>2</sup> reaching from 97.9 to 99.2 per cent. of the total in three hours (Table I.). When, however, the linseed was acidified to represent digestive conditions, no hydrocyanic acid was evolved and similar negative results followed the use of pepsin and rennet in acid solutions. Even acids of one-hundredth normal strength prevent the enzyme from working, and hydrochloric acid of one-thousandth normal strength produces a slackening in the rate of evolution (Curve and Table). One-hundredth normal lactic acid only allows small fractions of the hydrocyanic acid to be evolved. Butyric acid appears to be less powerful, but this lack of power is due to the volatility of butyric acid, since at the end of the experiment one-half of the butyric acid had evaporated. It may reasonably be inferred that acidity of any sort prevents the action of the enzyme. Now all physiological authorities give the acidity of the human stomach-contents as about one-twentieth normal, the acidity being greater in dogs, and I have myself found that the acidity of fresh green grass is of about the same order. Under normal circumstances, therefore, linseed cannot produce hydrocyanic acid when fed to carnivorous or herbivorous animals, because the acid present in the stomach prevents the enzyme in the linseed from acting, but there might be some abnormal circumstances when linseed would become poisonous.

Amygdalin, though readily yielding hydrocyanic acid above 60° C. in presence of acids,<sup>3</sup> does not yield hydro-

\* <sup>2</sup> From Table by logarithmic interpolation,  $K = \frac{1}{t_2 - t_1} \log_e \frac{C_1}{C_2}$  (see *The Nature of Enzyme Action*, W. M. Bayliss).

<sup>3</sup> Caldwell and Courtauld, *Trans. Chem. Soc.*, 1907, 666.

cyanic acid at 45° C. in presence of hydrochloric acid. Small traces of hydrocyanic acid are yielded by amygdalin, pepsin and hydrochloric acid at 45° C. Mixtures of amygdalin and cotton seed or soy bean yield no hydrocyanic acid, but linseed or Rangoon beans when mixed with amygdalin, do yield hydrocyanic acid. A mixture of amygdalin (0.02 gramme) and linseed (0.1 gramme) yields in five hours 80 per cent. of the theoretical amount of hydrocyanic acid.

Linseed, therefore, contains an excess of enzyme, whereas a mixture of amygdalin and linseed (1 to 5) contains an excess of cyanogenetic glucoside.<sup>4</sup> In either case the evolution of hydrocyanic acid is stopped by acids, hindered greatly by cellulose, hay or straw, and hindered to a less extent by sugar, treacle, chloroform and benzaldehyde. On the other hand, a mixture of linseed and Rangoon beans yields slightly more hydrocyanic acid than the same substances separately. Some at least of the above variations are due to variations in the degree of acidity, but both the sugar and cellulose used were free from any trace of acidity, leaving no doubt that there are many other causes than acidity which may modify the rate at which hydrocyanic acid is evolved from linseed.

Should hydrocyanic acid be produced in the alimentary canal of an animal, the rate of production would have a most important bearing on the subject, since if produced slowly enough, the animal could remove it. The figures in Table I. show the constants of the velocity of reaction, which vary with the conditions.

Various samples of linseed and linseed cake have given varying quantities of hydrocyanic acid, when treated by the method described, but such quantities of hydrocyanic acid are greater than those yielded by simple steam distillation. Old samples of linseed meal contain acid and in consequence yield less hydrocyanic acid than they otherwise would.

<sup>4</sup> Compare *Auld. Chem. Soc. Trans.*, 1908, 1264.



In other experiments than those here described, air has replaced hydrogen, the rate has varied from 5 to 20 litres of gas per hour, and the temperature has been  $35^{\circ}\text{C}$ . instead of  $45^{\circ}\text{C}$ ., but the general tendency of the results has been in the same direction. By far the most convenient method for experimental purposes is the one here described, namely, ten litres of hydrogen per hour at  $45^{\circ}\text{C}$ .

Two experiments can be made at the same time by interposing at E in Fig. 1, first, a U-tube filled with "permanganate lime,"<sup>5</sup> to absorb vapours of benzaldehyde or other organic vapours; secondly, an evaporator like V, and lastly an absorber like B.

*Summary.*—The amount of hydrocyanic acid yielded by linseed and the rate at which that hydrocyanic acid is yielded, depend upon the amount of cyanogenetic glucoside, on the amount of enzyme, on the temperature, on the degree of acidity of liquid present and on the presence or absence of a large number of other substances.

Under the circumstances of animal digestion, the acidity is of the highest importance. With normal health, the acidity of the stomach is too high to allow linseed to evolve hydrocyanic acid, but there may be abnormal circumstances when the production of hydrocyanic acid would set in.

The above research explains the paradox that whilst a farmer considers linseed one of the safest cattle foods and uses it for calf-rearing, yet the chemist shows that linseed in the laboratory readily gives off prussic acid, one of the most deadly poisons.

Further, this research suggests a possible explanation of certain rare and puzzling cases of cattle-poisoning. Should a linseed, rich in cyanogenetic glucosides, be fed to a beast suffering from indigestion, of such a peculiar character that the food was not rendered acid, then prussic-acid-poisoning might set in. Such a combination of circumstances must be very rare but is by no means impossible.

<sup>5</sup> Made by mixing lime, potassium permanganate and potassium hydrate, moistening with water, drying and granulating.

TABLE I.

RATE OF EVAPORATION OF HYDROCYANIC ACID BY 10 LITRES OF HYDROGEN  
PER HOUR FROM 50 C.C. LIQUID AT 45° C.

KCN + 20 HCL.				LINSEED, CALCUTTA.			
Mins.	HCN Mgm.	%	Velocity Constant.	Mins.	HCN Mgm.	%	Velocity Constant.
16	·225	31·5	·024	29	·110	29·0	·012
33	·430	60·2	·032	80	·273	72·0	·018
52	·555	77·7	·030	125	·349	92·0	...
83	·644	90·1	·028	237	·384	101·0	...
136	·695	97·5	...	300	·384	...	...
199	·708	99·2	...				
300	·708	99·2	...				
Taken	·714						
KCN + 100 HCL.				LINSEED CAKE.			
Mins.	HCN Mgm.	%	Velocity Constant.	Mins.	HCN Mgm.	%	Velocity Constant.
16	·230	32·2	·024	23	·000	0	0
33	·430	60·2	·031	59	·057	12·8	·004
52	·554	77·6	·030	125	·210	47·1	·007
83	·641	89·8	·025	314	·393	88·1	·008
136	·690	96·6	...	366	·446	100	...
199	·699	97·9	...				
300	·699	97·9	...				
Taken	·714						
LINSEED, CALCUTTA.				LINSEED, LA PLATA.			
Mins.	HCN Mgm.	%	Velocity Constant.	Mins.	HCN Mgm.	%	Velocity Constant.
26	·103	27·5	·012	24	·022	11·4	·005
61	·243	64·0	·021	61	·079	41·0	·011
122	·333	87·6	·017	148	·164	85·0	·016
195	·370	97·4	...	236	·193	100	...
305	·374	98·5	...	291	·193	100	...
LINSEED, CALCUTTA.				LINSEED, CALCUTTA, AND $\frac{N}{100}$ BUTYRIC ACID.			
Mins.	HCN Mgm.	%	Velocity Constant.	Mins.	HCN Mgm.	%	Velocity Constant.
26	·100	26·3	·012	23	0	0	0
61	·243	64·0	·020	51	·023	6·0	·0022
122	·336	88·5	·019	125	·125	32·9	·0046
195	·372	98·0	...	216	·243	63·7	·0068
305	·382	100·5	...	300	·317	83·5	·0094

LINSEED, CALCUTTA, AND $\frac{N}{200}$ HCl.				LINSEED, CALCUTTA, AND $\frac{N}{1000}$ HCl.			
Mins.	HCN Mgm.	%	Velocity Constant.	Mins.	HCN Mgm.	%	Velocity Constant.
24	0	0	0	24	·043	11·4	·0050
59	·024	6·3	·0019	61	·193	51·1	·0160
130	·104	26·8	·0035	148	·340	89·9	·0181
225	·191	50·3	·0041	236	·365	96·6	...
325	·272	71·6	·0056	291	·365	96·6	...

LINSEED, CALCUTTA, AND $\frac{N}{100}$ LACTIC ACID.				LINSEED, CALCUTTA, AND $\frac{N}{500}$ HCl.			
Mins.	HCN Mgm.	%	Velocity Constant.	Mins.	HCN Mgm.	%	Velocity Constant.
23	0	0	0	21	·010	2·6	·0012
51	0	0	0	62	·133	35·0	·0098
125	·022	5·8	·0008	138	·300	78·9	·0154
216	·055	14·5	·0011	234	·373	98·1	...
300	·086	22·6	·0012	299	·376	98·9	...

$$\text{Velocity Constant, } k = \frac{1}{t_2 - t_1} \log_e \frac{C_1}{C_2}$$

## A WATER-SEALED CONSTANT-PRESSURE HYDROGEN GAS GENERATOR.

By S. H. COLLINS.

[Read November 24th, 1911.]

In some work on the rate of evolution of hydrocyanic acid, it became necessary to generate pure hydrogen at a steady rate of ten litres per hour. Many forms of apparatus were employed, with the result that a new system was perfected.

The chief advantages of the apparatus here described are that:—

- (1) The pressure of the gas can be easily varied over a wide range.
- (2) Air cannot possibly diffuse in through rubber connections, etc.
- (3) The zinc need not be granulated, but only broken into lumps.
- (4) Economy of acid.
- (5) Simplicity, unbreakability and compactness.

In Fig. 4 (page 108) A is a Winchester quart bottle delivering dilute sulphuric acid (1:8 by volume) at constant level D, C is a tap for shutting off acid at night. The wooden block B provides the coarse adjustment, the air tube in A provides the fine adjustment for pressure of gas. The wide tube D is roughly graduated in centimetres, counting the level of the sprinkler F as zero. The working pressure of gas reckoned in terms of a column of dilute sulphuric acid, can be seen at any time. The cork block E fastens the tube D to the inverted cylindrical jar J, two or three turns of copper wire making the connection a semi-rigid one. The large glass bottle K serves to hold the waste acid and also, in conjunction with the jar J, serves as a gas-holder to maintain regularity

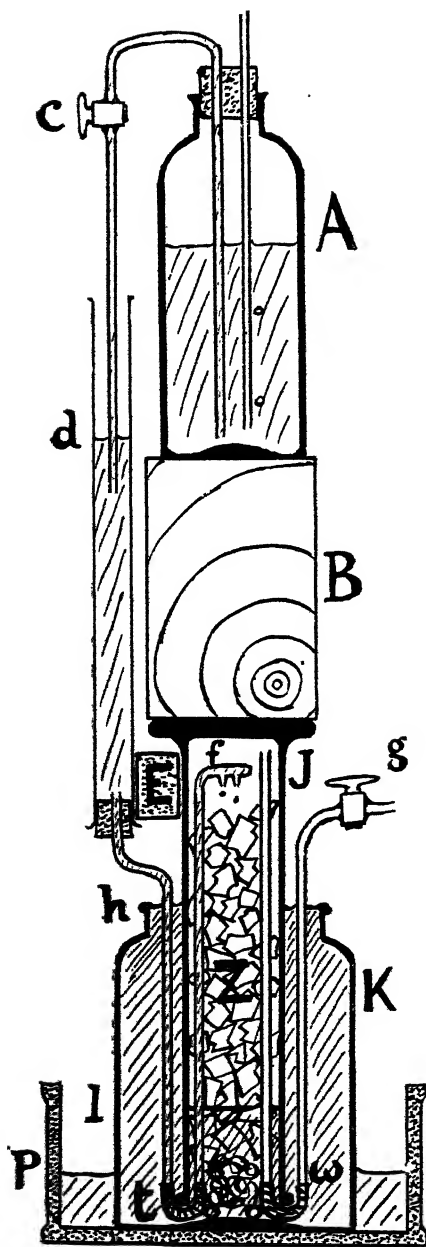


FIGURE 4.

of gas supply. The pneumatic trough P receives the waste acid after it has done duty. From time to time the trough is emptied by syphon or otherwise. The lumps of zinc are represented by Z, which rest upon a ball made by tangling some copper wire. Between the mouth of the jar J and the bottom of the bottle K are two pieces of wide rubber tube to form a cushion and prevent breakage. It is convenient to attach these pieces permanently to the jar J, by a copper wire. The acid supply tube has a rubber connection at T and the gas-delivery tube has a similar rubber tube at W. These rubber tubes should be much narrower than the tubes used as a cushion for J, otherwise the weight of the zinc and acid might close them. The height from L to H measures the pressure of the gas in terms of saturated zinc sulphate solution, hence HL is only about  $\frac{3}{4}$  DF. Three corks are hammered into the mouth of K to fix J firmly. Evaporation takes place in P causing zinc sulphate to

crystallise out and firmly cement K to P. A little hot water will at any time remove this zinc sulphate if required. The zinc and the trough are heavy and bring the centre of gravity of the whole apparatus low down, thus providing stability.

It is convenient to have the bottle A in duplicate with rough marks at 2,000 c.c. and 2,300 c.c. Water up to the 2,000 mark is put into the spare bottle, strong sulphuric acid poured to the 2,300 mark, and the fresh bottle of acid put up in place of the bottle which has become exhausted without causing any interference with the flow of gas. The jar J holds about 7 kilograms of zinc and only needs recharging at long intervals. For recharging, A and B are lifted off, the three corks in the mouth of K removed and the jar J slowly lifted. When the bulk of the waste liquid has drained off, the jar J is stood on its proper foot with the tube D hanging below the level of the table. The copper wire ball is removed and the zinc poured in.

The hydrogen obtained was quite free from oxygen, but contained sulphuretted hydrogen, arsenuretted hydrogen, and perhaps phosphuretted hydrogen and acetylene. Bubbling a gas through liquids renders pressure control very difficult and rubber connections were undesirable. To get over the difficulty a new absorbing agent was used. If about 3 parts of powdered mercuric chloride and 1 part of lime be mixed, made into a paste with water, dried, broken up, sieved and the convenient sized lumps bottled, a very fine absorbent for all the impurities can be obtained. This "mercury lime" needs only one tube and therefore few connections, works rapidly, and shows the progress of the absorption of impurities by turning first yellow, then black.

# A COMBINED GOVERNOR AND GAUGE FOR MAINTAINING A REGULAR FLOW OF GAS, AND A THERMOSTAT WITH DELICATE ADJUSTMENT AND LONG RANGE.

By S. H. COLLINS.

[Read November 24th, 1911.]

In the course of some investigations on the rate of evaporation of hydrocyanic acid gas from aqueous solutions, a regular flow of gas was required and it became necessary to use gas-governors and pressure gauges. At first the apparatus used in testing coal-gas was used, but proved too clumsy for the special use to which it was put. Ultimately a simple glass apparatus was devised, which is now described (Fig. 5).

A is a glass tap with long pointer and scale mounted on wooden block, B, C and M are rubber connections, D is a piece of glass rod drawn out with a long tail, E is a piece of glass Sprengel tube blown with a bulb at one end and then ground down, F is a float weighted with mercury and having a platform of flat glass cemented on, K is a piece of wide glass tube and J is a glass cylindrical jar. The point of entry of the gas is at N and the point of exit at X. When in work, the pressure of the incoming gas depresses the water in the pressure tube to I, but the gas does not pass through this tube, but passes on into the chamber containing the valve made by D and E. The rate at which the gas passes through this valve depends upon the position of the float F, which is kept hovering about a position determined by the level H according to the exact dimension of the instrument. The level of water G is dependant on the amount of water placed in the jar J and is easily adjusted before operations commence. The height GH is in consequence fixed once for all, the height GI shows the pressures of the incoming gas, the height HI shows the surplus pressure which is being got rid

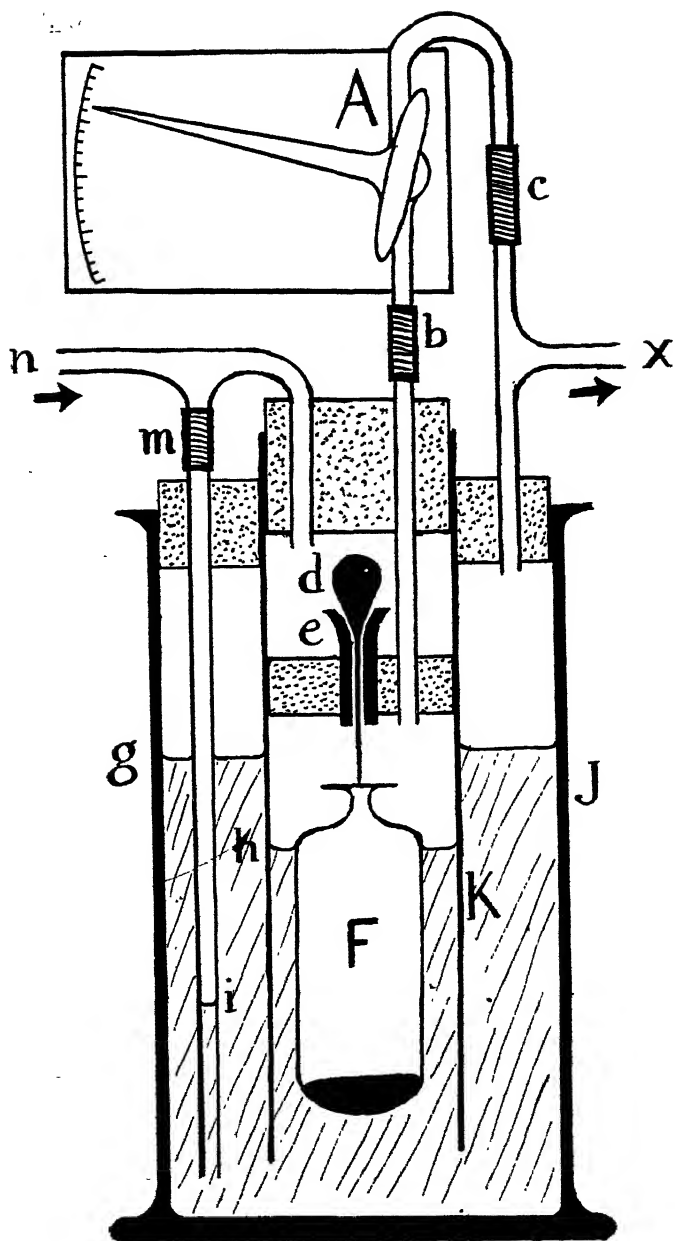


FIGURE 5.



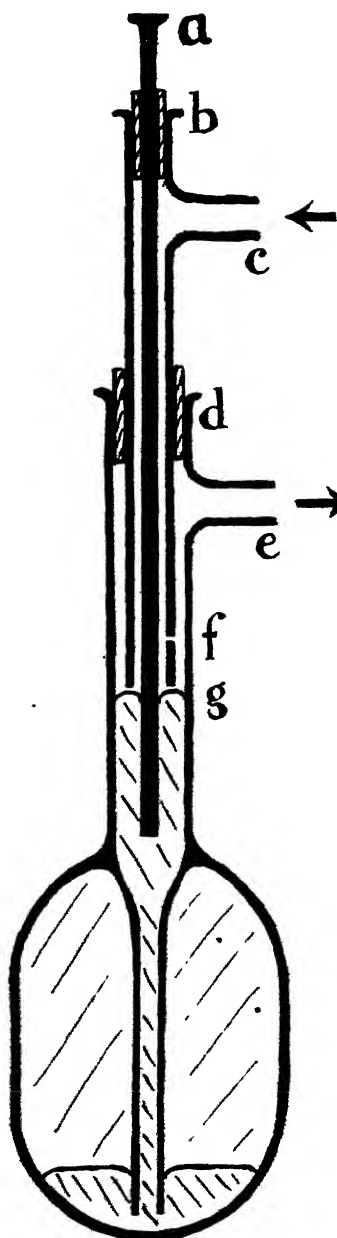


FIG. 6.

of by the valve DE, and which is liable to variations due to irregular action in the other parts of the apparatus.

As the difference of pressure on the two sides of the tap is kept constant and the tap is fixed by trial, both pressure and resistance are constant and therefore current is constant also, unless the specific gravity of the gas should vary. Within certain limits the pressures and resistances before N and after X may vary but the current of gas remains constant.

The records from twenty-two actual runs with this instrument show an average flow of  $10.05 \pm .22$  litres of gas per hour; when 10 litres was the flow required. This rate includes stopping and starting and long intervals of one or two hours without attention.

In diagram of the thermostat (Fig. 6), A is a thin glass rod, C is a T-piece with bye-pass at F, B and D thin strips of writing paper twisted two or three times round, and the remainder of the apparatus the ordinary body of a thermostat.

The rod A serves as the fine adjustment and renders unnecessary the restriction commonly placed at G. The rod and tubes fit one another fairly closely so that the cross

section of mercury at G is small. The close fit is rendered possible by the use of paper coils at B and D instead of corks. Experience shows that these paper coils are quite gas tight. The T-piece C serves as coarse adjustment, gas-inlet, and by-pass. The bulb contains mercury and toluene or other organic liquid with high co-efficient of expansion. The bulb may be made long and narrow if required. The thin glass rod A may be replaced by a knitting needle.

In use the T-piece C is approximately adjusted and then the rod A moved up and down for fine adjustment. Actual records of 215 observations gave an average temperature of  $45^{\circ}04\text{ C.} \pm .10$  for  $45^{\circ}\text{ C.}$  intended.

## MODERN THEORIES OF NUMBER CONSIDERED AS THE MEASURE OF CONTINUOUS QUANTITY.

BY PERCY J. HEAWOOD.

[Read November 11th, 1911.]

In the whole range of mathematical enquiry, there is perhaps no subject which is in some aspects so simple and practical, in others so complicated and baffling, as that which deals with modern theories of number as used for the representation of continuous magnitude, and with their application to the theory of functions. It is not, indeed, only in the realm of pure mathematics that the contrast between the continuous and the discrete has led to puzzling questions. In the domain of physics, dealing with the ultimate constitution of matter, we resolve the continuous mass into a number of separate atoms: then again, not content with this analysis, we sometimes seek to explain the atom as a portion of some ultimate fluid endued with vortex motion or otherwise differentiated, thus thinking of the ultimate as continuous. Still, on the whole, it is the resolution of the continuous mass into constituent particles which has proved

most fruitful. And now it seems that in the realm of pure mathematics likewise, we are to consider the continuous as best represented, for many purposes at all events, in terms of the discrete.

We may, indeed, begin by thinking of a quantity  $x$ , which may take any value, as suitably represented by a distance from a fixed point on a straight line; and  $y$ , a function of  $x$ , as representable by a graph. This is a most helpful conception, perhaps unduly disparaged in the modern theory; but when we come to consider the actual expression of  $y$  in terms of  $x$ , questions soon arise in connection with which the idea of  $x$  as represented indifferently by any lengths whatever on a straight line seems confusing and inadequate. Thus, to take an obvious illustration: if  $y = a^x$  where  $a = -1$ , and  $x = \frac{p}{q}$ ; the function is imaginary if  $p$  is odd and  $q$  is even; it is real and negative if  $p$  and  $q$  are both odd; it is real and positive if  $p$  is even and  $q$  is odd; while yet we may have fractions of these different kinds as near together in value as we please. Thus the values of  $y$  entirely depend on what we may perhaps term the arithmetic structure of  $x$ , and will be totally different for values which will be represented on the line by points so close together as to be undistinguishable. To take a less extreme instance, suppose  $y = a^x$ , where  $a$  is positive. The values of  $y$  then run continuously for different forms of fractional index, but still we are dependent for an interpretation of  $a^x$  on a definite fractional value of  $x$ . In what sense then can we say here that  $x$  may take all possible values? What in fact are we to make of a value such as  $\sqrt{2}$  for  $x$ ? The common sense consideration that we have only to take  $\sqrt{2}$  to a sufficient number of decimal places, to get as close an approximation as we please to the corresponding value of the function, agrees practically with the result of the most refined analysis; but can we thus justify offhand the use of  $\sqrt{2}$  in such a connection? And then generally the question arises as to what we really ought to include, when we say that  $x$

can take all possible values, what right we have to treat  $\sqrt{2}$  as a definite number at all, or how in fine we know that such a number exists. It is, of course, easily proved that there can be no fraction whose square exactly equals 2, or indeed any integer  $m$  not included in the series of square numbers 1, 4, 9 . . . The fact that we can geometrically construct a length equal to  $\sqrt{m}$  by Euclid I.-47 makes the idea of such a measure of the length of a segment familiar; but does this justify us in treating  $\sqrt{2}$  as a number in other connections, as, for instance, in the measurement of time? And, further, what is the position of such transcendental numbers as  $e$  and  $\pi$ ? To make room for such quantities in the scheme of number on a purely arithmetic basis is the object of the modern theory; and for this two methods have been employed, that of *sections* due to Dedekind, and that of *sequences* which is Cantor's. Starting with the aggregate of integers and fractions, positive and negative, as a basis in each case, these are classed as the Rational Numbers. They have a perfectly definite order of magnitude and their laws of combination may be taken as known. Then, adopting Dedekind's method, we take a new entity called a Real Number, to be defined by a division of the Rational Numbers into two sets, such that every rational number has a place in one or other set, and all of the one set are greater than all of the other. Thus we may divide the rational numbers into two sets according as their squares are greater than 2 or less than 2; and this is taken to define a *real* number, which is in fact  $\sqrt{2}$ . In this case the rule is very simple. To define a number such as  $\pi$  would be more complicated; but in any case in which it would be possible, in some definite manner, to put any rational number whatever into an upper or a lower class, a real number is defined by the division of the classes. It must be noticed that real numbers corresponding to the *rational* numbers are not excluded: a possible division would be into numbers  $> 2$ , and numbers equal to or less than 2. The real number thus defined will correspond to the rational number

fig. 1.

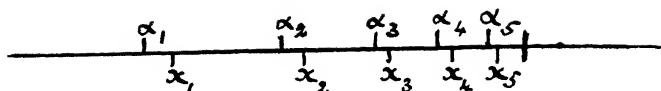


fig. 2.

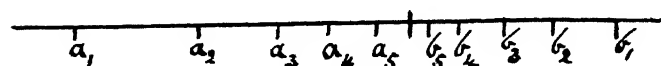


fig. 3.

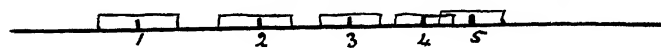


fig. 4.

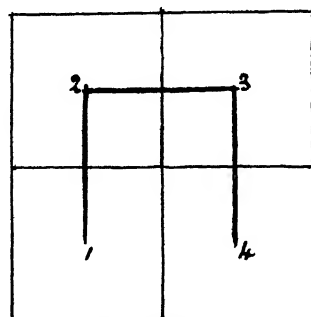
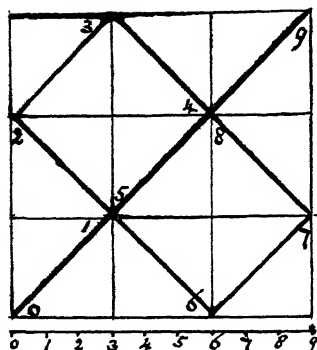


fig. 5(a).

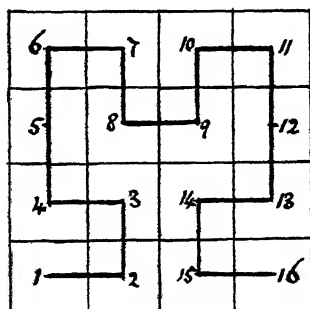


fig. 5(b).

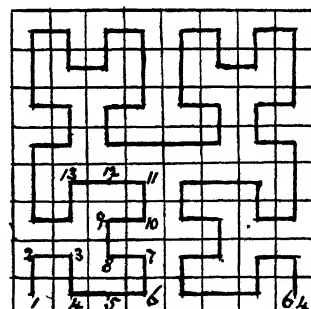
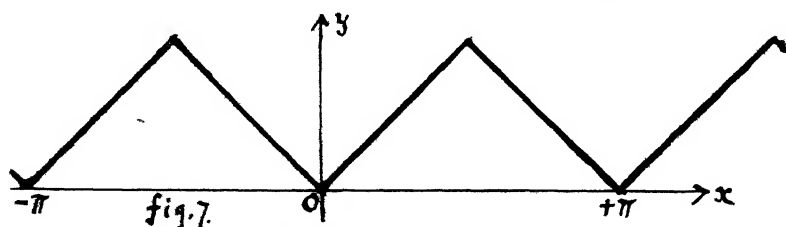


fig. 5(c).

fig. 6.



2 (which will stand either at the top of one class, as above, or at the bottom of the other). This is the method of Dedekind's *Schnitte*.

Cantor, on the other hand, defines a real number as the limit of a convergent sequence of rational numbers  $x_1, x_2, x_3, x_4 \dots$ ; such a sequence being convergent if, by taking  $n$  large enough, we can secure that  $X_n - X_{n+m}$  is less than  $\epsilon$ , an arbitrary small number, for all values of  $m$ . Again, numbers corresponding to the rational numbers are not excluded. The real number corresponding to 2, for instance, may be considered as defined by the sequence 2, 2, 2, 2 . . . . . or by the sequence  $1, 1\frac{1}{2}, 1\frac{3}{4}, 1\frac{7}{8} \dots$  which converges to the same value. Whichever method is adopted, the above are to be taken purely as *definitions*. They are not statements that anything otherwise definable exists, intermediate between the two classes in the former case, or as the limit of a sequence in the latter. They are to be regarded in fact as extensions of the domain of numbers beyond what is contemplated in arithmetic; and the point is, as in all similar extensions, that if we adopt them as definitions we can go on to show that the things thus defined may be taken as obeying the same laws of combination as the rational numbers with which we start. We have first to show that real numbers thus defined can be arranged in a definite order of magnitude, and then to define what we mean by the sum, difference, product, quotient, etc., of such numbers: for instance, the sum of the numbers given by the sequences  $a_1, a_2 \dots$ ;  $b_1, b_2 \dots$  is defined as that given by the sequence  $a_1 + b_1, a_2 + b_2, \dots$ ; *i.e.*, a real number definable in like manner; and then we can go on to deduce the laws and show that the system forms a consistent whole. Either method has its special advantages, that of Dedekind defines each number in a unique manner; *e.g.*, the division of the rational numbers into those whose squares are  $> m$  and those whose squares are  $< m$  (used to define  $\sqrt{m}$ ) is perfectly definite; while Cantor's has the drawback that there are an endless number

of sequences defining the same real number. It is, however, the easier method on which to base the deduction of the fundamental laws. But the two may be shown to be equivalent, so that we may avail ourselves indifferently of either point of view. And when it is understood that real numbers defined in this limiting way obey the fundamental laws of algebra, we may denote a *real* number as well as a rational number by a single symbol  $a$ . It is to be noticed further that a convergent sequence  $a_1, a_2, a_3, \dots$  of *real* numbers leads to no new results, beyond those which are covered by convergent sequences of *rational* numbers. If  $a_1, a_2, a_3, \dots$  are irrational, we can find in between any two of them, however close together, real numbers corresponding to rational fractions  $x_1, x_2, x_3, \dots$  (Fig. 1). Then the sequence of real numbers  $a_1, a_2, a_3, \dots$  will, it is easily seen, define the same limit as the new sequence of real numbers  $\bar{x}_1, \bar{x}_2, \bar{x}_3$  (say), which is practically indistinguishable from the corresponding sequence of rational numbers  $x_1, x_2, x_3, \dots$  itself. We have then in the totality of real numbers thus defined a complete and well rounded whole. There is, however, nothing in the form of a sequence which shows very readily whether it defines a rational or irrational number. Why should the sequence  $1, 1 - \frac{1}{3}, 1 - \frac{1}{3} + \frac{1}{3^2}, \dots$  lead to the simple fraction  $\frac{3}{4}$ , while  $1, 1 - \frac{1}{3}, 1 - \frac{1}{3} + \frac{1}{3^2}, 1 - \frac{1}{3} + \frac{1}{3^2} - \frac{1}{3^3}, \dots$  leads to the transcendental number  $\frac{\pi}{4}$ ?

The most obvious sequences, however, are those by which a number is expressed, in the ordinary way, as a decimal-fraction (or, more generally, a radix-fraction). The terms of a sequence may (in accordance with Cantor's definition) be decimals carried successively to 1, 2, 3, . . . places, thus the number  $\pi$  may be represented by the sequence 3.1, 3.14, 3.141, 3.1415, 3.14159 . . . the terms of which are those actually used in practical calculations. In order that a *real* number may be defined in this way by a non-terminating decimal, we must suppose that the digit which occurs in

any place is determinable (at least ideally) by definite numerical processes, or in accordance with some definite law. The question has indeed been raised whether the number whose successive digits were determined by the casting of dice, could be considered as a real number, but it is held that such a number would not fulfil the conditions of the case. When a number is decimally expressed it is rational if, and only if, the digits from and after some fixed point are periodic, otherwise irrational. The terminating decimal may be brought into the periodic class by expressing it as a circulator whose period is 9. Thus  $\cdot 5$  is the same thing as  $\cdot 49$ .

For theoretical purposes other scales besides that of 10 are often convenient, and the ternary scale, in which each digit must be 0, 1, or 2, has been particularly employed.

But whether the method of Dedekind or of Cantor be adopted, we have a complete theory of irrational numbers developed on arithmetical lines out of that of rational fractions, independently of geometrical considerations, or of ideas of continuity based on intuition. Such a system is found to have many advantages in connection with the theory of functions, where the arithmetical structure of the numbers involved may, as we have seen, be all-important. But it must be remembered that, even so, our system is not really independent of ideas of continuous quantity, so long as the fraction is defined in the usual way; for the division of a unit into  $q$  equal parts implies an absolutely continuous quantity to be thus divided. And so, in the extreme determination to be independent of all such ideas, the theory of fractions has been revised in what we cannot help regarding as a hopelessly artificial manner. We cannot pursue this in detail, but must just say generally that fractions are then defined as entities to be inserted between the integers, with a relative order of magnitude assigned in an artificial way, and laws of addition, etc., laid down in an arbitrary manner; according to which, however, it is shown that we have a self-consistent system. The laws are, of



course, those which hold for fractions as ordinarily understood, and would hardly have suggested themselves otherwise. Surely this is running a questionable idea to death.

But, leaving any criticisms for the present, we have to consider how the system of real numbers we have reached in this purely arithmetical way is adequate to the representation of continuous magnitudes, *e.g.*, the distances, measured from a fixed point, of all points on a line. In tracing such a correspondence, it has been proposed to evade difficulties in the theory of measurement, by the principle that four harmonic numbers may be consistently made to correspond throughout to four points forming, geometrically, a harmonic range, a relation definable in a purely descriptive way; but, even then, the language of measurement is practically used.

We may therefore think of the fraction  $\frac{p}{q}$  as corresponding to the  $p^{\text{th}}$  point of division of a unit length divided into  $q$  equal parts, and for practical purposes it is easily seen that the rational numbers alone are sufficient to define the position of points on the straight line to any required degree of accuracy. The aggregate of rational numbers is in fact everywhere dense, in the sense that between any two, however near together, an indefinite number of others can be inserted; and so there is no interval on the straight line, however small, in which there are no "rational" points, *i.e.*, points represented by rational numbers. But no rational numbers will *precisely* represent the "irrational" points, for which geometrical theory prepares us. Such points, however, may be looked at as the limits of sequences of rational points corresponding to sequences of rational numbers (by which, as we have seen, "real numbers" are defined). In this way all the real numbers are brought into correspondence with all the points on the straight line. Thus it is claimed that the real numbers, though defined in a discrete way, are adequate for the complete analytical representation of continuous magnitude, and their aggregate is therefore

called the Arithmetic Continuum. It has to be realised that infinite as is the aggregate of the rational numbers, the aggregate of the *real* numbers is an infinity of infinities above them in extent. Indeed they illustrate a very important distinction, which is fundamental in the development of the theory, between numbers which are countable, or enumerable, and numbers which are not. Numbers are said to be countable, not only when they are finite in number so that the process of counting comes to an end, but when, being infinite in number, they can be arranged in some definite systematic order in which any assigned number of the total will sooner or later occur. In this sense the integers 1, 2, 3 . . . are obviously countable. Not only so, but the rational fractions  $\frac{p}{q}$  may be arranged in countable order. For we may take successively the cases where  $p+q=2$ , then  $p+q=3$ , then  $p+q=4$ , and so on; arranging the fractions under each head,  $p+q=n$  (say), in order of ascending integral values of  $q$  from 1 upwards (omitting fractions which have already occurred in lower terms). Thus under  $p+q=7$  we have in order  $\frac{6}{1}, \frac{5}{2}, \frac{4}{3}, \frac{3}{4}, \frac{2}{5}, \frac{1}{6}$ . In the complete series thus arranged,  $\frac{1}{1}, \frac{2}{1}, \frac{1}{2}, \frac{3}{1}, \frac{1}{3}, \frac{2}{2}, \frac{1}{4}, \frac{3}{2}, \frac{2}{3}, \frac{1}{5}, \frac{4}{1}, \frac{3}{3}, \frac{2}{4}, \frac{1}{6}, \frac{5}{1}, \frac{4}{2}, \frac{3}{5}, \frac{2}{6}, \frac{1}{7}, \frac{6}{1}, \frac{5}{3}, \frac{4}{4}, \frac{3}{6}, \frac{2}{7}, \frac{1}{8}, \frac{7}{1}, \frac{6}{4}, \frac{5}{5}, \frac{4}{7}, \frac{3}{8}, \frac{2}{9}, \frac{1}{10}, \frac{8}{1}, \frac{7}{5}, \frac{6}{7}, \frac{5}{9}, \frac{4}{10}, \frac{3}{11}, \frac{2}{12}, \frac{1}{13}, \frac{9}{1}, \frac{8}{6}, \frac{7}{8}, \frac{6}{11}, \frac{5}{12}, \frac{4}{13}, \frac{3}{14}, \frac{2}{15}, \frac{1}{16}, \frac{10}{1}, \frac{9}{7}, \frac{8}{9}, \frac{7}{14}, \frac{6}{15}, \frac{5}{16}, \frac{4}{17}, \frac{3}{18}, \frac{2}{19}, \frac{1}{20}, \frac{11}{1}, \frac{10}{8}, \frac{9}{13}, \frac{8}{16}, \frac{7}{19}, \frac{6}{20}, \frac{5}{21}, \frac{4}{22}, \frac{3}{23}, \frac{2}{24}, \frac{1}{25}, \frac{12}{1}, 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\frac{11}{402}, \frac{10}{411}, \frac{9}{420}, \frac{8}{429}, \frac{7}{438}, \frac{6}{447}, \frac{5}{450}, \frac{4}{450}, \frac{3}{453}, \frac{2}{454}, \frac{1}{455}, \frac{49}{1}, \frac{48}{46}, \frac{47}{89}, \frac{46}{98}, \frac{45}{107}, \frac{44}{116}, \frac{43}{125}, \frac{42}{134}, \frac{41}{143}, \frac{40}{152}, \frac{39}{161}, \frac{38}{170}, \frac{37}{179}, \frac{36}{188}, \frac{35}{197}, \frac{34}{206}, \frac{33}{215}, \frac{32}{224}, \frac{31}{233}, \frac{30}{242}, \frac{29}{251}, \frac{28}{260}, \frac{27}{269}, \frac{26}{278}, \frac{25}{287}, \frac{24}{296}, \frac{23}{305}, \frac{22}{314}, \frac{21}{323}, \frac{20}{332}, \frac{19}{341}, \frac{18}{350}, \frac{17}{359}, \frac{16}{368}, \frac{15}{377}, \frac{14}{386}, \frac{13}{395}, \frac{12}{404}, \frac{11}{413}, \frac{10}{422}, \frac{9}{431}, \frac{8}{440}, \frac{7}{449}, \frac{6}{458}, \frac{5}{460}, \frac{4}{460}, \frac{3}{463}, \frac{2}{464}, \frac{1}{465}, \frac{50}{1}, \frac{49}{47}, \frac{48}{91}, \frac{47}{100}, \frac{46}{109}, \frac{45}{118}, \frac{44}{127}, \frac{43}{136}, \frac{42}{145}, \frac{41}{154}, \frac{40}{163}, \frac{39}{172}, \frac{38}{181}, \frac{37}{190}, \frac{36}{200}, \frac{35}{209}, \frac{34}{218}, \frac{33}{227}, \frac{32}{236}, \frac{31}{245}, \frac{30}{254}, \frac{29}{263}, \frac{28}{272}, \frac{27}{281}, \frac{26}{290}, \frac{25}{300}, \frac{24}{309}, \frac{23}{318}, \frac{22}{327}, \frac{21}{336}, \frac{20}{345}, \frac{19}{354}, \frac{18}{363}, \frac{17}{372}, \frac{16}{381}, \frac{15}{390}, \frac{14}{399}, \frac{13}{408}, \frac{12}{417}, \frac{11}{426}, \frac{10}{435}, \frac{9}{444}, \frac{8}{453}, \frac{7}{462}, \frac{6}{471}, \frac{5}{480}, \frac{4}{480}, \frac{3}{483}, \frac{2}{484}, \frac{1}{485}, \frac{51}{1}, \frac{50}{48}, \frac{49}{93}, \frac{48}{102}, \frac{47}{111}, \frac{46}{120}, \frac{$

lie in magnitude between  $a_1$  and  $b_1$ , and suppose  $a_2$  less than  $b_2$  (whether  $a_2$  or  $b_2$  actually occurs first). Then again we may suppose  $a_3, b_3$  to be the next two which occur in the interval  $a_2, b_2$  and  $a_3 < b_3$ ; and so on indefinitely. Then each of the sequences  $a_1, a_2, a_3 \dots b_1, b_2, b_3 \dots$  will define a real number as its limit (the same or different). But such a limiting number can never occur in the countable order, owing to the way in which the  $a$ 's and the  $b$ 's are selected as the *next* numbers in the successive intervals; so that in the last interval constructed at any stage no preceding number in the countable order can have occurred. Suppose that the limiting number does occur somewhere. As we must sooner or later get past *any assigned number* in the countable order, we sooner or later reach an interval (containing the limit) in which the supposed number does not occur. The countable series of numbers then cannot include all the real numbers, since it cannot include the limit in question.

Thus the real numbers are more than countable, a conclusion which carries with it many important results. For instance, it helps to explain how it is possible that a continuous straight line can be adequately represented by an aggregate of separate points, of which it might be said that an infinite number can occupy no space. This would be a valid objection to the idea of its equivalence to any *enumerable* set of points, but the idea of an *unenumerable* infinity alters in a remarkable way the validity of any such argument. In fact we may define the "measure" of a set of points on a straight line in a way which emphasises this distinction. If we suppose all the points of any set to be enclosed each in a small interval (Fig. 3), the intervals being diminished indefinitely according to any law, and if we take the limit of the sum of all these intervals (omitting overlaps), then the absolute minimum of such a sum, for all possible ways of choosing the intervals, may be taken as the measure of the set of points. (There is a condition over which we must not pause, which is in fact satisfied in

all cases which ordinarily arise.) Now if we take all the rational points on a segment, or all the points of any enumerable set, the measure is zero; for we may take the corresponding intervals to be of lengths  $\frac{\epsilon}{2}, \frac{\epsilon}{2^2}, \frac{\epsilon}{2^3} \dots$  and the sum of the non-overlapping parts of these will always be less than  $\epsilon$ , however far the series is prolonged. Thus the limit, when  $\epsilon$  is indefinitely diminished, must be zero. The measure then is certainly zero, although the points are everywhere dense in the straight line. On the other hand, the *real* points of a segment cannot possibly be enclosed in intervals from which any part of the segment is omitted, and the measure of the set of real points is the length of the segment itself.

It is a curious corollary from the general theory that the points on a straight line (of unit length, suppose) can be brought into correspondence with all points within the area of a square described on the straight line, although space of two dimensions is here involved. The general principle is as follows:—Any point on the straight line may be represented (as we have seen) by a non-terminating radix fraction, in the scale, say, of 3. If we form two new radix fractions, the one by taking the even digits and the other by taking the odd digits of the former number, these two will again be non-terminating radix-fractions, which will serve as the co-ordinates of a point within the square. It is seen how in this way the correspondence may be brought about, though a slight modification is needed to secure that every point on the straight line without exception is made to answer to at least one point within the square, and that all points within the square are included. The modified result, due to Peano, may be represented geometrically. Supposing a point to traverse the straight line continuously, a point which passed simultaneously through the corresponding points within the square would in the same time traverse every point of the area of the square moving along a definite path. Fig. 4 illustrates how this curious result

works out, by showing an early stage of a construction which would have to be carried on *ad infinitum* to represent the path. There we have a square divided into nine smaller squares, and the successive figures from 0 to 9 show how we may pass from one corner of the larger square to the opposite one by traversing in succession diagonals of the nine squares. If each of the nine squares be conceived as divided again into nine, and diagonals drawn in a similar manner, it appears that we could in a similar way pass from the first corner to the last by traversing diagonals of 81 squares. We have to suppose this process of division and diagonal construction repeated indefinitely, to obtain the path of the moving point corresponding to Peano's representation. Fig. 5 (*a*, *b*, *c*) shows three stages in another method of construction due to Hilbert, which if repeated indefinitely would lead to another form of what has been sometimes described as a "space-filling curve," though objection has been taken to this designation. Whatever may be said of the name, the idea is sufficiently curious, and is noticed as illustrating one of the paradoxes of the subject.

Passing on to practical developments, we notice that the fundamental idea that all the values of a continuously varying quantity may be adequately represented by the aggregate of real numbers suggest two important possibilities; the one is the *restriction* of the field of the variable, the other the *extension* of the idea of the function. If the values of the variable are regarded as discrete quantities, we may, if we please, make a selection including or excluding as many as we please. For instance, in considering the function  $y = (-1)^x$  we might reject all the values which we found to be awkward, and even so the values which are left will be everywhere dense; in other cases we may include all the rational numbers. More frequently we merely exclude from the aggregate of real numbers a finite or enumerably infinite series of values. In any such case the set of values which we retain is called the domain of the variable, and one of the

points of the theory (certainly of more theoretical than practical interest) is the result that any *perfect* set of points, as it is called, will do as well as the whole straight line for the domain of the variable  $x$ . A set of points is said to be perfect when it has two characteristics, one that all its points are *limiting points* or points having innumerable others within a distance however small, the other that it is *closed*, *i.e.*, that it includes in itself all limiting points definable by sequences of points belonging to it. It might be thought that nothing but the whole series of points in a finite segment or segments would fulfil such conditions, but this is not so. As an illustration, which is perhaps easier to grasp than the general principle, we may take the very artificial case of Cantor's typical non-dense perfect set (Fig. 6). If we divide a given segment into three equal parts, and blacken the middle segment; and then blacken the middle third of each of the two segments which are left; and then of each of four, and so on *ad infinitum*; the points which are left *not internal* to any of the black intervals (as they are technically called), *i.e.*, the external and end-points of the black intervals, form the perfect set in question. For although there is no space on the line however small which will ultimately be free from black intervals, there will on the other hand be no point of the set which will not have innumerable others in its immediate neighbourhood. Moreover, all limiting points must belong to the set, as none can occur within the black intervals. It therefore fulfils the requirements of a perfect set, and can be shown to be suitable for the domain of the variable.

But if the domain of the variable may be thus limited, whether in a natural or artificial manner, the theory suggests a corresponding enlargement of the idea of the function. The values of the variable being thought of as separate numbers, we may regard a function as determined not necessarily by any uniform law, but by any method which will assign a definite value of the function for each value of the variable within the domain. Thus such arbitrary examples have been given as that of a function which has the value zero for

each rational value of the variable, and the value unity for every irrational value; or which for all values of  $x$  between 1 and  $\frac{1}{2}$  is equal to  $\frac{x}{2}$ , while for values between  $\frac{1}{2}$  and  $\frac{1}{3}$  it is equal to  $\frac{x}{3}$ , between  $\frac{1}{3}$  and  $\frac{1}{4}$  it is  $\frac{x}{4}$ , and so on. It must be recognised, however, that all examples are not of this artificial character, and it was the discovery (in connection with Fournier's Theorem) that a convergent trigonometrical series, might, for different ranges of values of  $x$ , represent what we should naturally class as different functions of  $x$ , which led to the general investigations embodied in the theory of functions of a real variable. To take a single instance, the series  $\frac{1}{4}\pi - \frac{2}{\pi}\left(\cos 2x + \frac{1}{3^2}\cos 6x + \frac{1}{5^2}\cos 10x + \dots\right)$  represents for general values of  $x$  the ordinates of the broken line shown in Fig. 7. It is such facts which give practical interest to what is in many of its developments a somewhat arbitrary and very artificial theory.

We have thus attempted to indicate the main features of a large and difficult subject. To examine in any detail its bearing on the theory of functions would require a paper to itself. We must therefore be content to generalise.

The most obvious point is that there are many functions for which it is important to have a definite conception of the arithmetic structure of the values of the variable or variables which may be involved. Then, the freedom to define a function in different ways, for different numerical values, helps to avoid difficulties at awkward points, especially those depending on infinities or zeros.  $\sin \frac{1}{x}$ , for instance, becomes unmeaning when  $x=0$ . But if we define a function as 0 when  $x=0$ , and  $\sin \frac{1}{x}$  for all other values of  $x$ , we have a function which is clearly defined for all values of the variable. The most noticeable result, however (in the general theory), of the freedom to specify in an arbitrary manner the different values of a function, is the expenditure of what one is almost tempted to regard as

misplaced ingenuity, in the inventions of strange and monstrous forms, which behave as far as possible differently from the way in which a function might be expected to behave; so that the subject has been in fact described as the Pathology of Functions. On the whole, the development of its results is affected rather by the precision necessary to guard against such functional vagaries, than by anything directly arising out of the arithmetical theories on which it is based. As it is readily shown that for a continuous function the value of  $f(x)$ , where  $x$  is the limit of the sequence  $x_1, x_2, x_3 \dots$  must be the same as the limit of the sequence of values  $f(x_1), f(x_2), f(x_3) \dots$ , the values of such functions for irrational values of the variable are made to depend on those where  $x$  is rational, and so for these practically important functions many possible complications disappear. So far, however, does the subject revel in monstrosities, that by what might seem a misuse of language the functions employed in ordinary analysis and in its applications to Geometry and Physics, the ordinary well-behaved functions, are treated as exceptions, and abnormality ascribed to them, because they are characterised by regularities which functions, in the widest sense, do not in general possess. Indeed, the unsoundness of the logical basis of the ordinary theories of functions is supposed to be demonstrated by the fact that they do not apply to certain kinds of functions, which might well be explicitly excluded from the domain of ordinary analysis.

Whatever, again, may be the advantages of a complete arithmetical theory of irrational number, the determination to be independent of all ideas of continuity as given by intuition, in its logical developments, seems forced and unnatural; and this is seen particularly in the artificial and laboured treatment of fractions which it involves.<sup>1</sup>

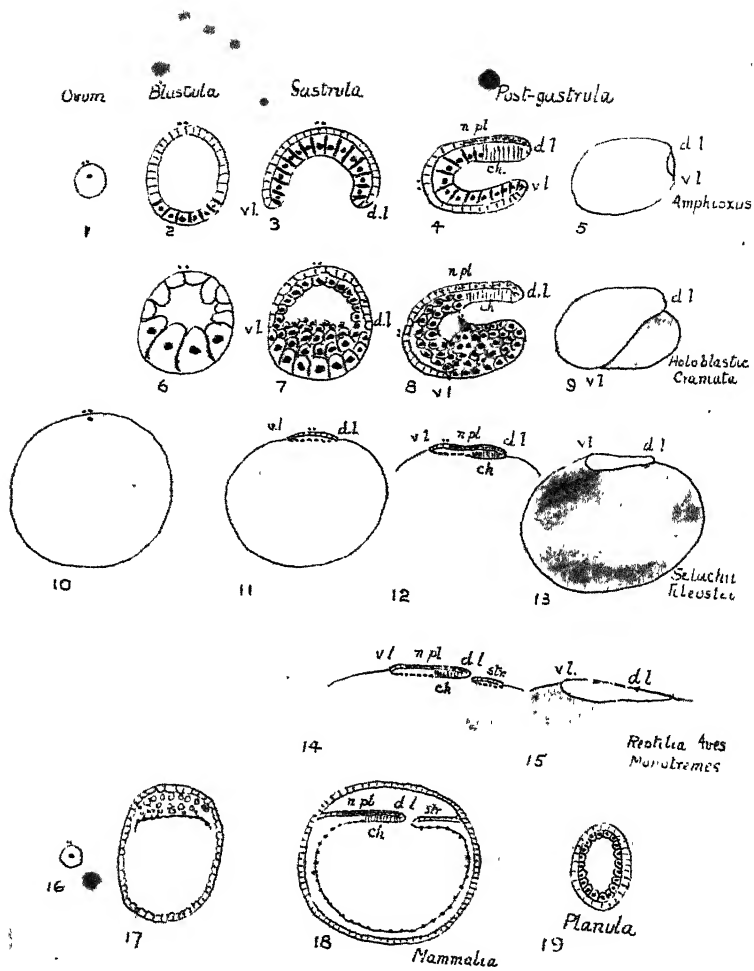
<sup>1</sup> It is a curious commentary on the supposed perfection of the logical basis of the purely arithmetical theory of the real number, that much controversy has arisen as to what after all the real number is; some holding that it is merely a sign, while others *identify* it with the class of rational numbers which define it!



And indeed the difficulty in the *proof* of the existence of a limit of a convergent sequence seems due to the same cause. It cannot be *proved* arithmetically, because the arithmetical expression of the limit may involve a new kind of number. Intuitionally the fact might be regarded as obvious. It is part of the same tendency that the conception of a function as (ideally) representable by a graph is so strongly disparaged. Yet many of the possible peculiarities of even a continuous function, which it is claimed make graphical ideas and methods misleading, can be at least realised, if not represented, in this way; as, for instance, the possibility of an infinite number of fluctuations (large or small) occurring within an indefinitely small space, as is the case for the function  $\sin \frac{1}{x}$  (before referred to) in the immediate neighbourhood of the origin. Moreover, the essence of some of the characteristic proofs of the modern theory of functions is most easily grasped when they are translated into graphical language.

At all events the conception of a continuously varying magnitude is in some respects simpler than that of any of the, necessarily more or less clumsy, arithmetical representations of it; it has a position of its own in the logic of the subject; and we might almost imagine that, when newer methods have done their work, there might be a certain reaction in favour of ideas derived from the intuitional continuum, as playing an important part in the logical basis of the whole.





EARLY STAGES IN THE DEVELOPMENT OF THE VERTEBRATES.

## EARLY STAGES IN THE DEVELOPMENT OF THE VERTEBRATES.

By ALEXANDER MEEK.

[Read February 27, 1912.]

Hubrecht in 1908<sup>1</sup> in a paper of exceptional merit based on his far-reaching discoveries in Mammalian embryology, stated that only one of the Chordate series attained its gastrula condition by invagination, viz., *Amphioxus*, and that all the others reached the same stage by delamination. The purpose of this short paper is to support Hubrecht in his contention and to show that in the Craniata the delamination is not directly comparable with the same process in the Coelenterata, but is a change founded on gastrulation by invagination, and rendered necessary by the accumulation of yolk in the entodermal cells.

In the case of *Amphioxus* the segmentation of the ovum results in the formation of a blastula (Fig. 2). The blastula consists of a single layer of cells including a cavity, the segmentation cavity. This is the structure of the Coelenterate blastula, and this may be assumed to be the characteristic first stage of the Metazoa. The proplanula or blastula becomes two layered by delamination or invagination. In the latter case the cells at the vegetal pole are invaginated, obliterating more or less completely the segmentation cavity, the opening formed by the invagination being called the blastopore. In the former case an invasion of cells takes place into the interior of the sphere, and these become arranged to form the entoderm (Fig. 19). The segmentation cavity in this instance is converted into the enteron and a blastopore is formed by the breaking down of the cells at the vegetal pole.

<sup>1</sup> *Early Ontogenetic Phenomena in Mammals*. Q.J.M.S. n.s., v. 53. See also the succeeding papers by Assheton and by MacBride.

In *Amphioxus* as in the simple Ascidians the gastrula is formed by invagination, but as soon as we pass into the realm of the Craniates we find that the accumulation of yolk in the entodermal cells—an early expression of increase in size—invagination is prevented. A delamination of cells takes place into the interior, resulting in the formation of a primitive gastrular enteron (Figs. 6 and 7). The blastopore, however, occupies its Chordate position and is widely distended by the entodermal cells which have failed to be invaginated. The dorsal lip as in *Amphioxus* and in the Ascidians early manifests its Chordate characteristics, growing backwards, yielding a continuation of the primitive ectoderm and neural plate, and of the primitive entoderm with the notochord and mesoderm. The whole of the rest of the blastopore, while not taking any share in the formation of the segmental structures, by its growth backwards yields a similar continuation of ectoderm and entoderm with an intervening vascular mesenchyme.

It is plain now with regard to the primitive enteron that two alternatives, and two only, are possible. If the dorsal layer of delaminated entoderm becomes continuous with the ectoderm at the dorsal lip of the blastopore then the enteron will be directly continuous with that later contributed by the secondary growth of the blastopore. If, however, it maintains its association with the ventral entoderm, a fresh communication must be established by the breaking down of the intervening entodermal cells. This is what takes place in such holoblastic Craniates as *Petromyzon*, and evidently usually in the Frog. Even in the meroblastic *Hypogeophis* the primitive enteron is thus put into communication with the secondary enteron. At all events it is clear that what has been called the segmentation cavity in all these forms is really the primitive enteron.

A further increase of yolk, again associated with the larger size of the animals, led to the typical meroblastic conditions where the segmentation was confined to the animal pole of the egg. In this case a blastula properly speaking

cannot be formed, since the yolk part of the egg does not participate in the formation. There results from the segmentation a group of cells which by delamination are resolved into an upper ectoderm and an underlying dorsal entoderm. The blastopore is marked by the edge of this mass of cells now occupying a small area on the yolk which so widely, so to speak, distends the mouth (Fig. 11). There are now no underlying or ventral entodermal cells, and the primitive delaminated entoderm is continuous with the ectoderm, and consequently the primitive enteron becomes continuous with that formed by the dorsal lip of the blastopore. Furthermore, there is a tendency exhibited in the Selachian development to precociously unite the upper portion of the rest of the blastopore which, as has been stated, yields the vascular mesenchyme.

The discovery of the unsegmented yolk was thus associated with an early manifestation of considerable progress, as we may gather from a consideration of the living examples of the Selachians and the Teleostei. And it must have taken place very early in Craniate phylogeny. The method of progress was rediscovered at the Amphibian level, and led to the enormous developments illustrated by the living and fossil reptiles and birds. Some of the early examples of these animals must have had immense eggs. Segmentation results in these as in Selachians and Teleostei in the formation by delamination of an ectoderm and an entoderm, but there is this difference, the tendency of the part of the blastopore below the dorsal lip to unite precociously already noted in the lower level of meroblastic eggs, takes place so early as to be practically dovetailed into the gastrulation. The vascular mesenchyme appears behind the dorsal lip in the form of a primitive streak and groove (Figs. 14 and 15), and the rest of the blastopore is thus left free to surround the yolk in ectoderm and entoderm. In all cases, as is well known, this portion of the blastopore besides its mesenchyme forming tendencies is concerned with the formation of the cloaca, and this is another reason for its being carried so early to the posterior aspect of the embryo.

After the work of Semon<sup>2</sup> and of Wilson and Hill<sup>3</sup> relating to the development of Monotremes, it is plain that the Mammalian condition has arisen as indeed van Beneden<sup>4</sup> stated in 1899 from a modification of the meroblastic type accompanying uterine development. In the Monotremes there is an early delamination of the meroblastic segmentation cells into ectoderm and entoderm, both of which rapidly invest the now much reduced yolk. The outer layer as in birds and reptiles becomes the serosa or false amnion, and the inner layer forms the entodermal covering of the yolk sac. In considering, therefore, the holoblastic segmentation of the small ova of the other Mammals, it is impossible to speak of blastula and gastrula. The results of segmentation are the formation of an outer envelope of cells including an inner mass of cells. Through the great growth of the former the latter becomes relegated to the animal pole and becomes differentiated into embryonic ectoderm and entoderm (Fig. 17). As soon as that takes place the procedure is precisely that of the preceding meroblastic groups (Fig. 18). It is tolerably plain, therefore, that the trophoblast or outer layer of ectodermal cells is homologous with the outer or serosa layer of reptiles and birds. In Mammals it forms the ectoplacenta.

This brief review of the early developmental phenomena in Chordates serves to indicate that there is a primitive gastrula from which the anterior portion of the head, and of the brain, and a certain part of the ventral region are derived; that the segmental structures posterior to this region are added by the dorsal lip or the area of the blastopore called by that name; and that an unsegmental ventral part is yielded by the ventral area of the blastopore which also affords the mesenchyme of the vascular area. It shows also that at an early phylogenetic period the increase in size which accompanied vertebrate evolution was met by an

<sup>2</sup> *Zool. Forschungsreisen in Australien Bd. 2, 1894.*    <sup>3</sup> *T. R. S., v. 199.*

<sup>4</sup> *Anat. Anz. Bd. 16.*

accumulation of yolk in the entoderm and the effect of this was to prevent invagination. The further demands upon the egg to provide for a still larger embryo led to the meroblastic conditions illustrated by the Selachii and the Teleostei, in which forms the yolk part of the egg is altogether unsegmented, and in consequence the "yolk plug" widely distends the blastopore. This brought about the rearrangement of the blastopore, the ventral contribution to the embryo and to the vascular mesenchyme having to be made nearer to the dorsal lip. The manifestation of this is still more plainly visible in Sauropsida and in Mammals, which latter have had without doubt a meroblastic origin. This is clear from morphological considerations, and also it may be claimed from the changes which occur even during the first stages of development.

In the accompanying figures the entoderm cells are indicated by nuclei and shading, and the unsegmented yolk by shading, the notochord (ch.) is represented by closely placed upright lines, the ectoderm cells are drawn without nuclei, and the neural ectoderm (n. pl.) is shown by dots .*v.l.*, *d.l.* = ventral and dorsal lips of the blastopore; *str.* = primitive streak. The animal pole is indicated by two dots, the polar bodies.

#### EXPLANATION OF PLATE.

Figs. 1 to 5, *Amphioxus* and also the *Ascidians*.

Figs. 6 to 9, *Holoblastic Craniates*. In fig. 8 the primitive enteron is separated from the secondary enteron as in *Petromyzon* at this stage.

Figs. 10 to 13, *Selachii* and *Teleostei*.

Figs. 14 and 15, *Reptilia*, *Aves* and *Monotremata*.

Figs. 16 to 18, *Mammalia*.

Fig. 19, The planula stage of *Coelenterata*, to be compared with fig. 7.



## THE GEOLOGY OF SOUTH-WESTERN FRANCE.

By E. GRAHAM CLARK, B.Sc.

[Read 14th March, 1911.]

The Rocks of South Western France, which belong almost entirely to the Tertiary Age, are of considerable geological interest, since they include excellent examples of certain beds, which are wanting in Great Britain, and are only rarely found elsewhere.

To deal with the entire geology of this district in one paper, however, is impossible, so that we will restrict ourselves to the land lying between the river Adour and the mouth of the Gironde. In this area, however, we will find an almost complete succession of the rocks laid down during the Tertiary period.

The Northern or Blayais district consists chiefly of the Eocene. To the south, round Bazas and to the east, round Libourne, the Oligocene is the predominating feature. Whilst to the west of Bordeaux we get the Miocene rocks, often covered over by the Pliocene and alluviums of a later period.

Towards the end of Cretaceous times, the whole of France and possibly the greater part of Europe lay under a shallow sea. It is probable that the disturbances which affected England at this time, also made themselves felt in France, and it is not unlikely that those two great mountain-ranges, the Pyrenees and the Auvergne, owe their origin to these great earth-movements. A great synclinal was thus formed, the sea still reaching far inland. To the north, the Cretaceous outcrop ran in a N.W. direction, whilst to the south, it again appeared at the foot of the Pyrenees in a line running E.W. It was between these two lines that the tertiary rocks were laid down. The sea floor of this great bay was

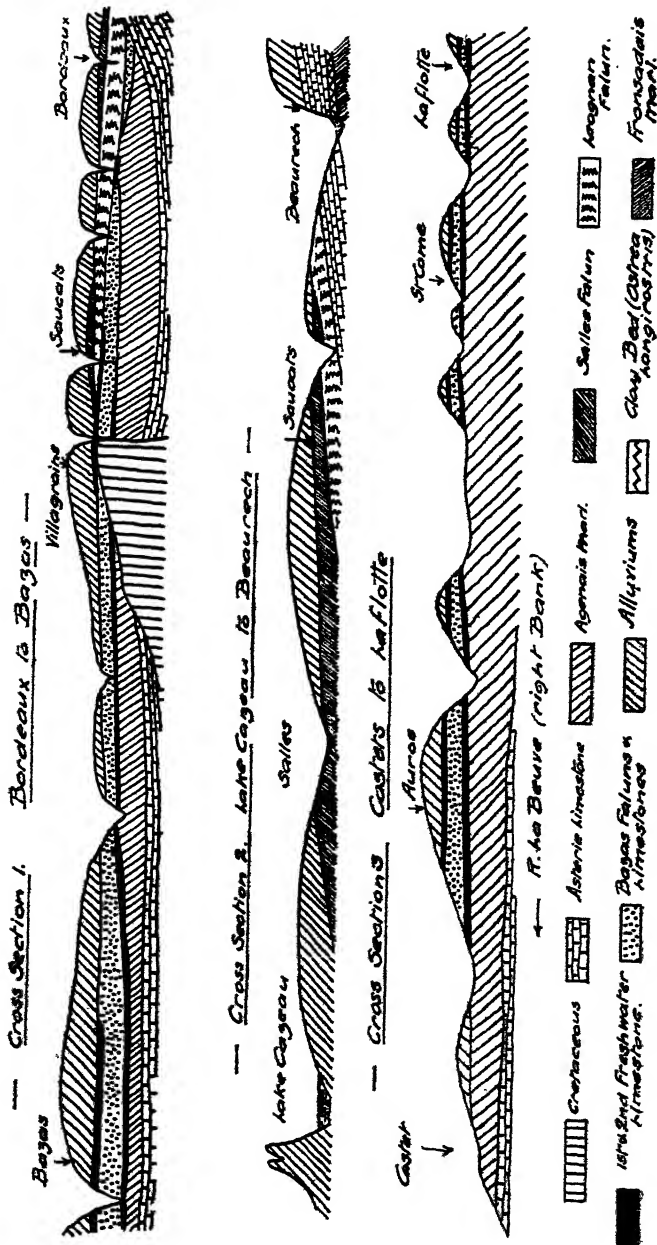


Fig. 1.

far from regular, and to this is due the fact that the Cretaceous may be seen at Villagrains and Landiras (south of Bordeaux), whereas at Bordeaux itself, it has not been struck even at a depth of 650 feet. Usually, however, the floor sloped down from east to west, and it is thus evident that the younger rocks of the tertiary lie to the west of the older ones.

The Eocene is exposed in the north in the neighbourhood of Blaye, and at Biarritz, Dax, Pau, etc., in the south. It is characterised by marine and freshwater limestones, sands and clays. The most important beds of the lower Eocene or Suessonien are the "Calcaire grossier de Blaye" in the north, and the nummulitic limestones in the south. The former is a coarse limestone much used for building purposes. It contains many Echinoids (*Echinolampas Stelliferus*, *E. Similis*, *Sculetta Cailliandi*, *Laganum Marginale*). The nummulitic limestones found at Biarritz, etc., are very similar to the beds which were laid down all over Europe at this period. There are four divisions to these beds, which may be distinguished by the following fossils:—(a) *Nummulites intermedia*, (b) *N. Complanata*, (c) *N. Varioloria* (found in the Plassac marls), (d) *N. Biarritzensis*. The classification, however, is not very satisfactory, and it is often very difficult to distinguish between the beds. The nummulitic formations have also been found in borings near Bordeaux, showing that these beds were very extensive.

The freshwater limestone of Plassac is the most important rock of the Bartonien or middle Eocene. The beds round Blaye are some 30 feet thick and consist of marly limestones, clays and sands. The fossils are for the most part freshwater (*Limnæ longiscata*, *Planorbis rotundatus*, *Crocidiliens* and *Palæotherium* teeth).

The Upper Eocene or Ligurien is represented by the St. Estephe limestone (near Blaye). It is about 50 feet thick and consists of limestones intermixed with clays. (*Sismondia*, *Echinolampas ovalis*, *Echinanthus Elegans*, etc.).

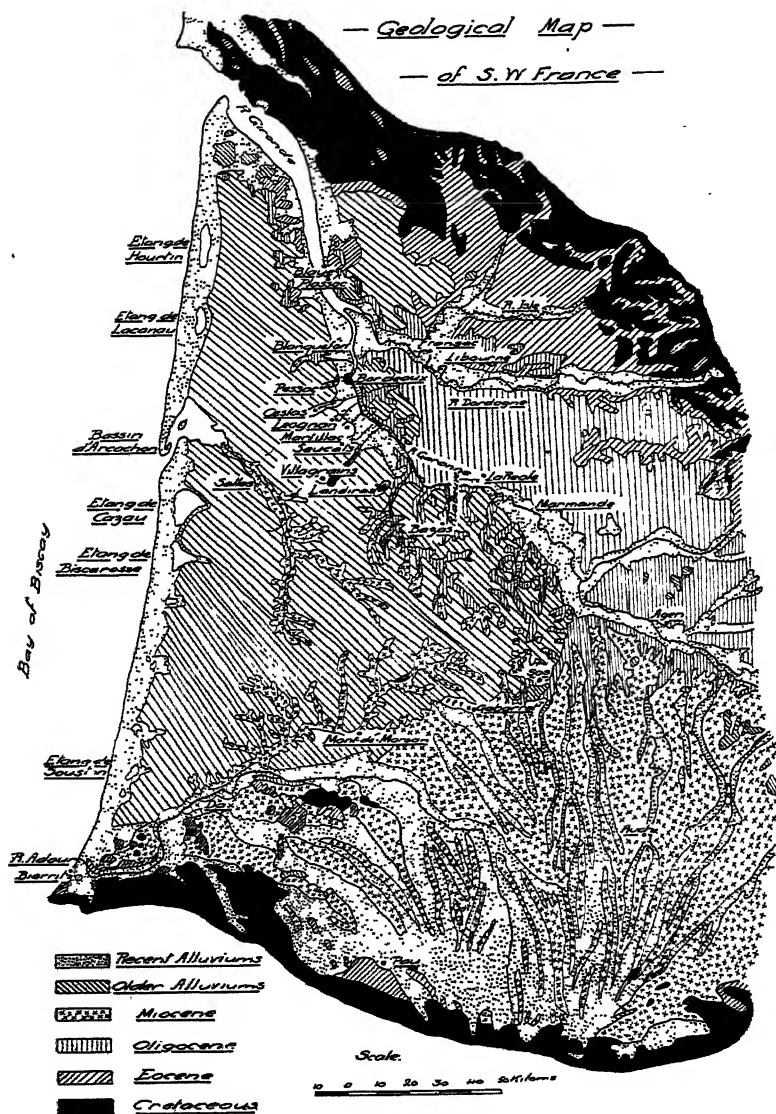


FIG. 2.

The Oligocene beds are best shown in the Libournais district, lying between the Dordogne and the Garonne. It is also well shown in the Bazadais, where it runs under the recent alluviums, but is exposed along the streams which flow into the Garonne.

The lower Oligocene or Tongrien, which corresponds to our Headon beds in the Isle of Wight, and to the Gypsum series in the Paris basin, consists mainly of marine limestones, marls and clays. In this district they attain a thickness of 170 feet and are characterised by the "Asterie" limestone, Castillon freshwater limestone and the Fronsadais marls. These last two are of little importance, the Castillon limestone only being a few feet thick. The "Asterie" limestone is, however, very extensive. It attains a thickness of some 130 feet, and is to be seen in a series of hills which run along the east bank of the Garonne. These hills are specially noticeable opposite Bordeaux. This formation is often intermingled with beds of clay and marl, which are very rich in fossils (*Natica crassatina*, *Turbo Parkinsoni*, *Pecten Bilandelli*, *Scutella striatula*, etc.). At its base is a clay bed noted for the many oysters found in it (*Ostrea longirostris*, also *Fimbria lamellosa*, *Chama lamellosa*, *Rostellaria fissurella*).

At the end of Tongrien times there appears to have been a period of marine regression, for it is noticeable that the lower Aquitanien beds are of freshwater origin. The freshwater lakes did not, of course, cover the whole country and it thus follows that the beds are not very extensive. The fossils are not numerous (*Cerites*, *Cyrenes*, *Potamides*).

The middle Aquitanien consists of clays and marls (marine). As there is no unconformity between the middle and lower Aquitanien, it is hard to draw any definite line between the two, the Bazas Sandstone and the Agenais (Agen) marl. At Bazas and La Reole, the beds attain a thickness of 300 feet. In some parts the fossils are fairly plentiful (*Cerithium plicatum*, etc.). The sea seems to have

withdrawn a second time at the end of the Oligocene (Upper Aquitanien) and we get another freshwater limestone formed similar to the previous one, which is of small importance.

The Miocene rocks which follow directly on the Upper Aquitanien do not show any unconformity, but before we deal with them it is necessary to mention the "faluns" which, though found in the Aquitanien (Bazas), are especially characteristic of Miocene times. The beds consist of a very soft sandstone, crumbling if touched and may be compared to the English crag found in the Pliocene. They are extremely abundant in fossils, and the sand, in fact, is composed almost entirely of sea shells, either broken or in some cases wonderfully preserved. These fossils belong chiefly to the Molluscs and seem to denote a very shallow sea under an almost tropical climate. The faluns are also very extensive in Touraine, but nowhere do they seem so well developed as in this district. The beds, in fact, present so many points of interest, that it is impossible to deal with them fully to-night, so that we will only consider them very briefly.

The Miocene is sub-divided into three stages, namely, the Burdigalien or Langhien, the Helvetien and the Tortोनien, the last of these being entirely wanting in this district. The Burdigalien is best known round Bordeaux, whereas the Helvetien is best developed in the south at Sos, Gabarret, Dax, etc. It is interesting to note that these two areas in which the Miocene occurs, correspond to those two synclinals which we noticed in the Cretaceous. The Burdigalien, in the north, is exposed by the small streams which run into the Garonne (Cestas, Leognan, Saucats). Here the beds consist of marls and sandstones, the fossils being very numerous, 400 different species have been distinguished at Leognan over a very small area (*Turritella terebralis*, *Pectunculus Cor*, *Buccium baccatum*, *Donax transversa*, *Cerethium papaveraceum*, etc., etc.). It will be noticed that most of these creatures cannot live at a depth greater than 15 fathoms and require a warm sea. Bones and teeth of larger animals

French Deposits.	Equivalent English Beds.	Characteristic Fossils.
<b>QUATERNARY</b> — Recent and Prehistoric Alluviums. Sands and gravels (Landes).		
<b>PLIOCENE</b> — Upper—Lignite deposits (Soulac). Middle and lower—Wanting.	Chillesford beds, Norwich crag, red crag. Coralline crag, etc.	
<b>MIOCENE</b> — <i>Tortonien</i> —Wanting. Faluns (Salles).  <i>Helvetien</i> —Marls (Martignas). Saucats and Cestas Faluns. <i>Langhien (or Burdigalen)</i> — Leognan Faluns. Leognan ossiferous marls.	Wanting.	Cardita Jouan- nette, Pecten- culus pilosus, Pecten Besseri. etc., etc. Lucina ornata, Natica burdiga- liensis, Oliva Basterote, Tere- bra plicaria, etc., etc.
<b>OLIGOCENE</b> —  <i>Aquitaniien</i> { Upper—Upper fresh-water lime- stone and fluvio marine beds (Bazas). Middle—Bazas marine sandstone Agenais marl. Lower—Agenais or lower fresh-water limestone. Agenais marl (lower). "Asterie" lime- stone. <i>Tongrien</i> { Castillon fresh- water limestone. Fronsadais marl.	Wanting.  Hempstead and Bembridge beds.  Headon beds.	Potamides and Congeria.    Natica crassatula. Turbo Parkinsoni. Scutella Striatula. Ostrea longirostris.
<b>EOCENE</b> — <i>Ligurien</i> —St. Esteph Limestone. Plassac fresh-water limestone. <i>Parisien</i> { Blaye limestone. Nummulitic beds. <i>Suessonien</i> —Nummulitic beds.	Barton clays.  London clay and Bognor beds. Oldhaven beds. Woolwich and Reading series. Thanet sands.	Ostrea and Anomia.  Lymnaea and Plan- orbis. Pecten—Ostrea.
<b>CRETACEOUS</b> — <i>Danien</i> —Landiras and Villa- grains limestone. <i>Senonien</i> —Villagrains limestone.		Ostrea vesicularis. Ananchytes orata, etc.

are also found (*Delphinus*, *Squaladon*). In the south, the Burdigalien is represented at Sos and Gabarret by clays, marls and freshwater limestones, and at Dax by faluns and sandy marls.

The Helvetien is exposed in a similar way to the previous beds. At Blanquefort (Bordeaux) it consists of grey red marls found on the banks of the Jalle. These marls are very rich in Echinoderms. In the valley of the Leyre, the formation is characterised by a yellow sand (*Menardi*, *Pecten solarium*, etc.), underlying beds of sands and clays (*Pecten latissimus*).

Throughout the formations with which we have been dealing we have often noticed beds of freshwater limestone overlying marine beds, thus showing that the land was continually undergoing changes in level. These movements, however, seem to have been very gradual, since the lower beds are in no way disturbed; this is very noticeable in the Miocene where some of the fossils are most beautifully preserved.

Since the Helvetien no further regular beds have been laid down and thus the Tortonien and Pliocene are wanting. During this time, the greater part of the land west of Libourne was covered by a loose sand and gravel.

Finally, we must mention the dunes which run along the sea coast and which are divided into two ages, namely, the older and the recent dunes. The former run perpendicular to the sea shore, whereas the more recent run parallel. The difference is probably due to the prevailing wind.



## A MODIFIED FORM OF THE LANDSBERGER BOILING POINT APPARATUS.

By J. H. PATERSON, M.Sc.

[Read 7th December, 1911.]

The apparatus described by Landsberger (Ber. 1898, 31, 458) and modified by Walker and Lumsden (J.C.S. 1898, p. 502) and further by McCoy (Amer. Chem. Jour., vol. 23, p. 353 [1900]) has many faults which make it difficult to use except in the hands of an expert operator. The following apparatus has been designed to give the operator a greater control over the concentrations of the solutions used and also to reduce to a great extent the bulk of the solvent.

The measuring vessel A is of the usual type but is enclosed in an outer jacket B furnished at the lower end with a hollow glass tap E having a hole of as large a diameter as possible. The solvent is boiled in a small extraction flask C and the vapour may be passed into the measuring vessel by means of the side tube S. To allow of the removal of the stopper from the top of the measuring vessel this tube has a ground glass joint at D. The elbow at F is continued upwards and closed by means of a tap or a pinch-cock and a piece of rubber tubing. The tube S may be, with advantage, covered with cotton or asbestos to prevent undue condensation of the vapour.

The glass tap should be greased with some substance not readily soluble in the solvent used. Glycerine has been found useful in the case of benzene and allied substances and vaseline for the alcohols.

*Method of Conducting the Experiment:* The boiling flask C is partly filled with the pure solvent and a few pieces of unglazed porcelain added to prevent bumping. The solvent is then boiled with the tap E open, until the whole of the

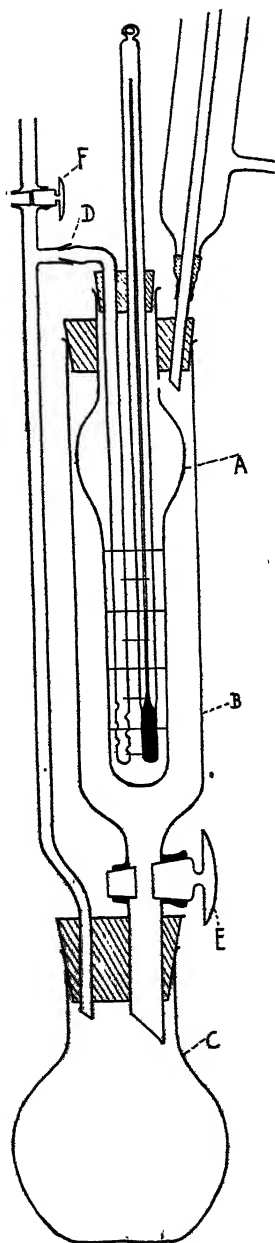


FIG. 1.

inner tube A is raised to the temperature of the boiling solvent, *i.e.*, until the solvent begins to drip back from the condenser. The tap is then closed, when the vapour will ascend the side tube and shortly the measuring vessel A will begin to fill with the liquid. When the thermometer registers a constant boiling point, the Bunsen burner is removed and the tap E simultaneously opened. The liquid which has collected above the tap flows back into the flask and causes a temporary cooling of the contents. This is sufficient to cause the solvent which has boiled into A to be sucked back into the flask.

A weighed quantity of the substance whose molecular weight is to be determined is then introduced into A and the tap carefully closed to such an extent that some of the vapour continues to pass up through it and warm the outer jacket, while the rest passes up the side tube D. When a sufficient quantity of the liquid has collected in the measuring vessel and a definite temperature is noted the tap E is again opened, but, to prevent the liquid from sucking back into the flask, the tap F is opened at the same time. The volume of the liquid and the temperature are then noted and the tap again partly closed.

The experiment is repeated at various dilutions until the measuring tube is filled, the readings being taken as before.

Benzene is a difficult solvent with which to get good results, as its latent heat of vaporisation is low compared with its boiling point. A fair test of the efficiency of the apparatus is therefore the results obtained in a molecular weight determination with benzene as a solvent.

*Experiment:* 65 grams of naphthalene were used (molecular weight=128). The thermometer used had a range of 50° and was graduated in 1/20 degrees.

Rise in B.P.	Volume of Solvent.	Molecular Wt.
1.6	10	133
1.05	15	135
.65	25	131

## THE ANALYSIS OF VINEGAR.

By J. H. PATERSON, M.Sc.

[Read December 1st, 1911.]

Solutions of the normal sodium or potassium salts of the majority of the fatty acids are alkaline to methyl orange and this fact makes it possible to estimate, with a little care, the quantity of such a salt existing in a given solution by a simple titration with standard alkali.

Normal malt vinegar contains, in addition to colouring matter and water, acetic acid and small quantities of sodium acetate and tartrate. If a normal vinegar is therefore titrated with standard alkali the quantity of acetic acid may therefore be directly determined. If this solution is then titrated back, using methyl orange as indicator, with a standard acid a slightly larger quantity of acid than alkali should be used owing to the presence of the original acetates and tartrates in the solution.

If, however, the vinegar has been previously adulterated with a mineral acid these acetates and tartrates will be decomposed and converted into free acetic and tartaric acids. On

titrating such a vinegar with standard alkali and then titrating back with standard acid it will be obvious that less acid will be required than alkali as the alkali salts of mineral acids are neutral to methyl orange. The difference, therefore, between the two titrations will give a measure of the mineral acid present.

The tartrates and acetates present in a normal vinegar may also be calculated either as sodium acetate or sodium tartrate from the difference between the two titrations.

*Method:* A sample of the vinegar is boiled under a reflux condenser with about one-fifth of its weight of animal charcoal (the charcoal is previously treated with dilute hydrochloric acid to remove all carbonates, well washed and dried for some time at  $110^{\circ}\text{C.}$ ). The liquid is then filtered and the interior of the condenser washed into the filtrate with some of the filtered liquor.

About 20 grams of the filtrate are then weighed out and diluted to 100 c.cs. with distilled water. Portions of 25 c.cs. are carefully titrated with  $\frac{N}{10}$  KOH, using phenol phthalein as indicator. The solution thus obtained is diluted to a known volume (about 100 c.cs.) and six drops of methyl orange added. Decinormal sulphuric acid is then run in until a pink colour without any yellow shade is produced.

A similar vessel is then taken and a volume of distilled water, equal to the titrated liquid in the first flask, placed in it. Six drops of methyl orange are added and the solution titrated with the decinormal acid till the colour matches that of the first flask. The quantity of acid required for this, subtracted from that required in the previous operation, gives the true volume of acid required for the back-titration of the sodium acetate.

Solutions containing known amounts of acetic acid, sodium acetate and sulphuric acid were analysed by the above method with the results stated below. (In Experiment V. a small quantity of alcohol was also added.)



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*With the Editor's Compliments.*



# THE ELASTIC DEFLECTION OF STEAM TURBINE ROTORS.

By J. MORROW, M.Sc., D.Eng.

[Read December 6th, 1911.]

1. *Introduction.*—The rotor of a turbine of the Parsons reaction type consists of a drum, to which the blades are fixed, and two spindles or shafts which transmit the weight of the drum to a bearing at either end. The deflection of the rotor when at rest is due to its own weight. Experiment shows that, when running, this deflection may vanish owing, possibly, to some time lag between the deformation and the stress to which it is due.

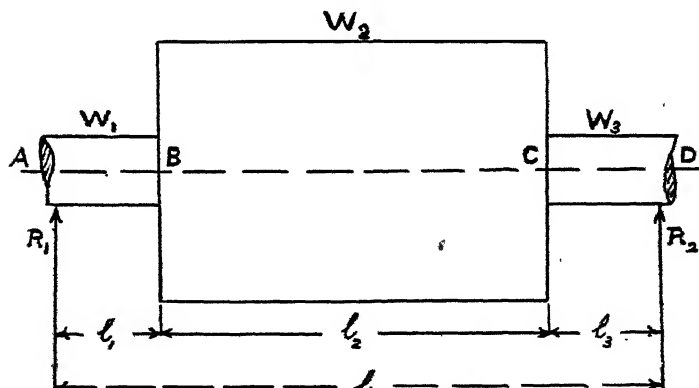


FIG. 1.

In the design of a steam turbine it is important that the static deflection of the rotor should not exceed a certain limit. It is usual, therefore, to estimate the deflection by means of an approximate formula; and it is the object of the present paper to enquire into the applicability of such formulæ and, by following the actual conditions more closely, to obtain more reliable expressions for the deflection. Let



the dimensions  $l_1, l_2, l_3$  be as shown in the diagram, the total length  $l$  being measured between the inner edges of the bearing metal. Let  $w_1, w_2, w_3$ , be the weights per unit length of the three portions of the rotor and

$$W_1 = w_1 l_1, W_2 = w_2 l_2, W_3 = w_3 l_3,$$

$I_1, I_2, I_3$  = the respective moments of inertia of the cross-sections about the neutral line,

$E$  = Young's modulus for the material,

$R_1, R_2$  = the reactions at the bearings as shown.

2. *Approximate Formulae*.—If the drum BC were perfectly rigid and if

$$l_1 = l_3 \text{ and } I_1 = I_3 (= I, \text{ say})$$

the shafts AB and CD would bend so that the drum, whilst remaining horizontal, would be deflected by an amount given by the ordinary formula for a beam of length  $L$  ( $= l_1 + l_3$ ) supported at the ends. On the assumption that the weight of the shafts is negligible compared with that of the drum, this deflection is

$$\frac{1}{48} \frac{W_2 L^3}{EI}.$$

On the same assumptions the deflection could be calculated equally well from that of a cantilever of length  $l_1$ , fixed at the end B and acted on by a force of  $\frac{1}{2} W_2$  at the free end A; the resulting deflection then being

$$\frac{1}{3} \frac{W_2 l_1^3}{2 EI}.$$

When, as in practice,  $l_1$  and  $l_2$  are unequal, the above expressions must be modified, and it is further necessary to take the weights of the shafts into account. After deflection the drum will not be parallel to its position in the unstrained state.

Two methods have been adopted to allow for these disturbing factors, the former of which is the more generally used. Either the deflection is calculated from the first formula with the substitution of the total weight  $W_1 + W_2 + W_3$  for  $W_2$ ,  $L$  remaining equal to the sum of  $l_1$  and  $l_3$ ; or the reaction  $R_1$  is calculated from the actual

weights and substituted for  $\frac{1}{2} W_2$  in the second formula,  $l_1$  then being the greater of the two lengths of shafting.

3. *Theory on the Assumption of a Rigid Drum.*—To obtain more accurate expressions we may, in the first place, assume the drum to be rigid and its centre of gravity to be at a distance  $a$  to the left of C in the diagram. Take the origin at A and let  $y$  be the deflection at any distance  $x$  along the centre line from A. Then, according to the Euler-Bernoulli theory, between A and B

$$EI_1 \frac{d^2 y}{dx^2} = -R_1 x + \frac{1}{2} w_1 x^2$$

and between C and D

$$EI_3 \frac{d^2 y}{dx^2} = -R_2(l-x) + \frac{1}{2} w_3(l-x)^2.$$

Integrating each of these equations twice, and determining the constants from

$$x=0, y=0; x=l_1, \frac{dy}{dx} = \theta;$$

and

$$x=l, y=0; x=l_1+l_2, \frac{dy}{dx} = \theta$$

in which  $\theta$ , (assumed small), is the inclination of the drum, we obtain the elastic central line of the displaced rotor.

Writing  $y_1$  and  $y_2$  for the deflections at B and C respectively, we then have

$$EI_1(y_1 - l_1\theta) = \frac{1}{3}R_1 l_1^3 - \frac{1}{8}w_1 l_1^4$$

and

$$EI_3(y_2 + l_3\theta) = \frac{1}{3}R_2 l_3^3 - \frac{1}{8}w_3 l_3^4.$$

But  $y_1$  and  $y_2$  are related to  $\theta$  by

$$y_2 - y_1 = l_2\theta,$$

and hence the following equation is arrived at, from which  $y_1$  may be calculated,

$$Ey_1 l = \left(\frac{1}{3}R_1 - \frac{1}{8}W_1\right)(l-l_1)l_1^3/I_1 + \left(\frac{1}{3}R_2 - \frac{1}{8}W_3\right)l_1 l_3^3/I_3 \quad (1)$$

In using this result,  $l_1$  should be taken as the greater of the two lengths of shaft, when  $y_1$  will be the maximum deflection. The value of  $y_2$  may be found by interchanging the suffixes throughout. In practice  $I_1$  and  $I_3$  are generally equal.

4. *Correction for Flexure of Drum.*—To examine the effect of flexure in the drum we must assume that it also accords with the Euler-Bernoulli theory. Then, from A to B,

$$EI_1 \frac{d^2 y}{dx^2} = -R_1 x + \frac{1}{2} w_1 x^2 ;$$

from C to D,

$$EI_3 \frac{d^2 y}{dx^2} = -R_2(l-x) + \frac{1}{2} w_3(l-x)^2 ;$$

from B to C,

$$EI_2 \frac{d^2 y}{dx^2} = -R_1 x + w_1 l_1(x - \frac{1}{2} l_1) + \frac{1}{2} w_2(x - l_1)^2 .$$

Writing  $\theta_1$  and  $\theta_2$  for the inclinations at B and C, these equations give:—

$$EI_1(y_1 - l_1 \theta_1) = \frac{1}{3} R_1 l_1^3 - \frac{1}{8} w_1 l_1^4$$

$$EI_3(y_2 + l_3 \theta_2) = \frac{1}{3} R_2 l_3^3 - \frac{1}{8} w_3 l_3^4$$

$$EI_2(y_1 - y_2 + l_2 \theta_1) = \frac{1}{2} R_1 l_1^2(l_1 + \frac{1}{3} l_2) - \frac{1}{2} w_1 l_1 l_2^2(\frac{1}{2} l_1 + l_2) + \frac{1}{8} w_2 l_2^3(4l_1 - \frac{1}{4} l_2) .$$

The third equation also provides:—

$$EI_2(\theta_1 - \theta_2) = \frac{1}{2} R_1 l_2(2l_1 + l_2) - \frac{1}{2} w_1 l_1 l_2(l_1 + l_2) - \frac{1}{8} w_2 l_2^3 ,$$

and from these we find that the additional deflection,  $y_a$ , to be added to that obtained from equation (1), is given by:—

$$EI_2 y_a \frac{l}{l_1 l_2} = (R_1 - \frac{1}{2} W_1) l_1 (\frac{1}{2} l_2 + l_3) + \frac{1}{2} (R_1 - W_1) l_2 (\frac{1}{3} l_2 + l_3) - \frac{1}{8} W_2 l_2 (\frac{1}{4} l_2 + l_3) . \quad (2)$$

This result shows that  $y_a$  is, under practical conditions, small but not necessarily negligible.

5. *Illustration and Comparison.*—The relative magnitudes of the various expressions for the elastic deflection may be illustrated by a numerical example. Thus, if  $l_1$ ,  $l_2$ ,  $l_3$  are respectively 50, 150 and 40 inches;  $W_1$ ,  $W_2$ ,  $W_3$  may be taken as 2,700, 50,000 and 2,160 lbs., and  $I_1 = I_3$  as 4,831, corresponding to a shaft of 18 inches external and 9 inches internal diameter. The reactions are

$$R_1 = 26,557 ; R_2 = 28,303 \text{ lbs.}$$

Taking  $E = 30 \times 10^6$  lbs. per square inch, equation (1)

gives  $y_1 = 0.00666$  inches; and equation (2) shows that this must be increased by  $218/I_2$ . If  $D$  is the mean diameter and  $t$  the thickness of drum, both in inches,  $I_2 = \frac{\pi}{8} D^3 t$ ; and taking this as 350,000, we get  $y_a = 0.00062$ , making a total deflection of 0.00728 inches.

Of the approximate rules given in the second section of this paper, the former makes the deflection 0.00575 and the latter 0.00764 inches. Experiment shows that the total deflection may include an appreciable amount of permanent set in addition to the quantities found above.

6. *Conditions at the Bearings.*—It is of interest to determine what amount of play is necessary at the bearings in order that the shaft may deflect as though merely supported.

If  $\beta_1$  is the inclination of the shaft, calculated as though supported, and  $b$  is the length of the bearing, the shaft will be free from constraint when the play or clearance exceeds  $b\beta_1$ .

For  $\beta_1$ , the above investigation gives:—

$$E\beta_1 = \frac{l_1^2}{I}(\frac{1}{2}R - \frac{1}{8}W_1) - \frac{l_1^3}{I_1 l}(\frac{1}{3}R_1 - \frac{1}{8}W_1) + \frac{l_3^3}{I_3 l}(\frac{1}{3}R_2 - \frac{1}{8}W_3).$$

In the numerical example, taking the length of the bearing surface as 24.1 inches, we obtain

$$b\beta_1 = 0.005 \text{ inch,}$$

so that the assumption of supported ends is in accordance with practical requirements.

It may be remarked that in this paper no allowance has been made for any possible lack of rigidity of the wheels which connect the drum to the shafts.

## A SURVEY OF THE GIRDLE STANES.

By G. R. GOLDSBROUGH, M.Sc.

[Read November 23rd, 1911.]

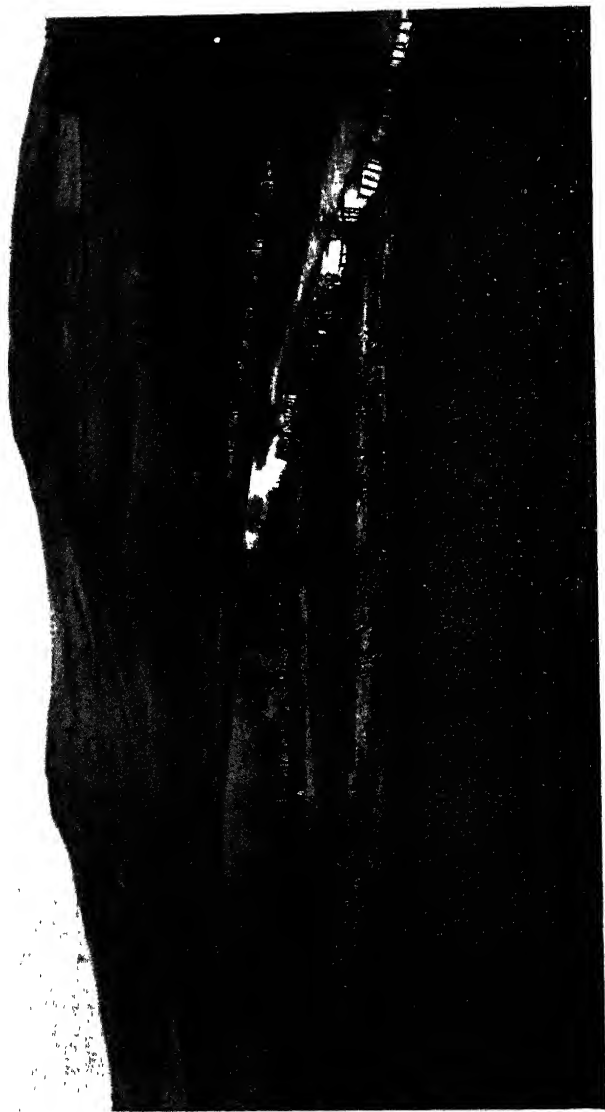
Lat.  $55^{\circ} 15' 14''$  N.

Long.  $3^{\circ} 10' 29''$  W.

I.—The Girdle Stanes are a standing stone circle in Eskdale, Dumfriesshire. The purpose of the survey, of which an account is here given, was to determine the practical purpose for which the circle was intended, and the date of its erection. The hypotheses at the base of the investigation are those of Sir Norman Lockyer, which are given in various papers read before the Royal Society and in his *Stonehenge*. A brief account of them is also given by Morrow in the *Proceedings* of this Society, III., 3, page 71. The consistency of the results obtained in the case of the Girdle Stanes goes far to justify the assumptions made.

II.—The Girdle Stanes stand in a hollow on the left bank of the White Esk about 13 miles above Langholm. The Circle is incomplete, a change in the course of the river having cut away part of the bank on which it stands and carried off many of the stones. There are 22 left, not counting some fragments which are obviously parts broken off from the larger stones. They are all very much weathered, many recumbent and some almost buried in the turf. No. 1 is the largest: it is 6 feet high and 12 feet in girth. No. 12 and No. 14 are both just over 4 feet in height. Nos. 3, 4 and 5 are 3 feet in height. No. 20 is  $3\frac{1}{2}$  feet in height and No. 2,  $3\frac{1}{2}$  feet. No. 19 is  $2\frac{1}{2}$  feet, and No. 8, 2 feet in height. No. 7 is a very large stone, though clearly not erect it is still  $5\frac{1}{2}$  feet above the ground. Nos. 6, 9, 10, 11, 13, 15, 17 and 18 are recumbent. Nos. 16, 21 and 22 are almost buried out of sight. The shape of the

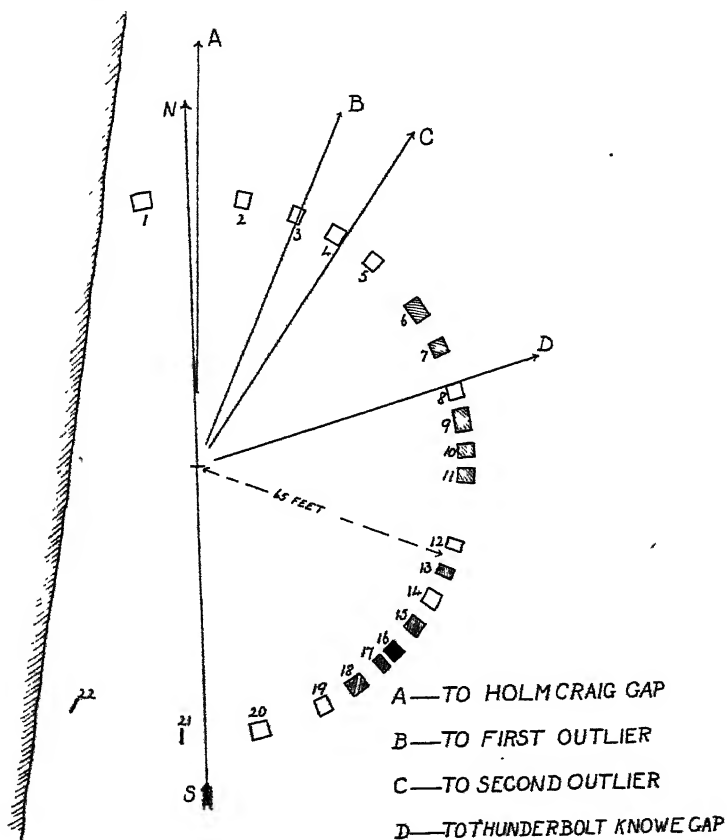




THE NORTH.

THE GIRDLE STANE.

Circle is fairly perfect. Its mean radius is 65 feet; when the centre had been found by trial, the chain taken round showed that no stone was out of its radial position by as much as 3 links. The diagram shows the true angular positions of the stones but not their true radial positions. No



## THE GIRDLESTANES

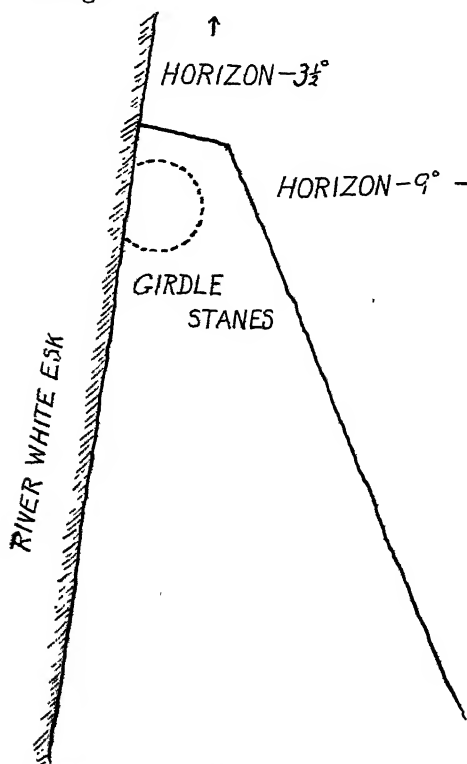
ESKDALEMUIR — DUMFRIESSHIRE

LAT  $55^{\circ}15'14''N$  . LONG  $3^{\circ}10'29''W$

FIG. 1.



attempt is made to show their shape, the conventional blocks giving their angular measurements as seen from the centre, which is all that is requisite. Those cross-hatched are recumbent, and those completely shaded are almost buried out of sight.



Rough sketch showing position of the Girdle Stanes at the head of a triangular holm.

FIG. 2.

The arc of the circle subtends an angle of  $221^\circ$  at the centre. If we suppose the three obvious gaps filled up—between 1 and 2, 11 and 12, 21 and 22—there would be 25 stones altogether in the remaining segment. The complete circle would on this basis have 40 stones. It is interesting to compare this with Dr. Morrow's survey of the Keswick Circle where there are 38 stones and 2 gaps. About 150 yards away, on the brow of a knove to the north-east and just visible through the turf, are two outliers. There is also a large number of other stones a short

distance away in a northerly direction, but quite invisible, owing to a rise in the ground, from the Girdle Stanes. Beyond these, no further stones could be discovered, and I was told by a neighbouring farmer who had ploughed all the land round about that he had found no others. The horizon requires some attention. At this point the Esk flows nearly due

south in a narrow valley between two, roughly parallel, chains of hills. To the north, looking along the river bed, the two chains appear to meet and bar the way owing to a turn in the valley. This forms a particularly well-marked hill gap, the Holm Craig—Clerk Hill Gap. To the north-east is the knowe mentioned above with the outliers on its brow. While to the east the land rises to the road and then steeply to the hill-tops, forming a very high eastern horizon. Here again, is a clearly marked gap—the Thunderbolt Knowe Gap. To the south is a long level holm, and the river with the hills beyond lies to the west. The whole effect is that the Circle lies low and has high land round it on the north and east. Beyond those mentioned, there are no further hill gaps sufficiently marked to be noticed and there was no conspicuous peak.

III.—In framing a method of attack, I decided that it would be best to take the bearings of all likely points—peaks, hill-gaps and outliers. Afterwards, at leisure, it would be possible to fit each into a scheme and those that had no meaning or value could be rejected. But it was first desirable to collect all the evidence and leave the sifting until later. With this view, after obtaining the true meridian from sun observations, I took the azimuths of the two outliers and the two hill-gaps mentioned above. The following are the particulars:—

CENTRE OF GIRDLE STANES TO—

		True Azimuth.	Altitude of Horizon.
I. Holm Craig—Clerk Hill Gap	...	N. 2° 18' 50" E	1° 50' 10"
II. First Outlier	...	N. 24° 5' 0" E.	3° 32' 30"
III. Second Outlier	...	N. 35° 7' 0" E.	3° 37' 20"
IV. Thunderbolt Knowe Gap	...	N. 74° 11' 40" E.	8° 58' 0"

With regard to the accuracy of these measurements, the first and last are very trustworthy, as the hill gaps are clear notches and at a considerable distance in each case. The second and third azimuths are subject to error. As has been said, the outliers are almost out of sight and probably recumbent; all that could be done was to take the mean positions of the visible portions.

The azimuths were reduced to declinations with the following results:—

CENTRE OF GIRDLE STANES TO—				Declination.	Object.	Date.
I. Holm-Craig—Clerk Hill Gap				36° 46' N.	Arcturus rising, Warning August Sunrise	1290 B.C.
II. First Outlier ... ..				34° 27' N.	Capella rising, Warning February Sunrise	1360 B.C.
III. Second Outlier ... ..				30° 3' N.	?	—
IV. Thunderbolt Knowe Gap ...				16° 5' N.	Sunrise	{ May 5th Aug. 9th

The last alignment marks with great accuracy two quarter days of the May year. A reversal of this line would give the sun-set point of the other two quarter days—November 7th and February 5th.

The first alignment marks the direction of the rising of Arcturus a short time before the sun-rise on August 9th, and so could be used to “warn” the priests of the approach of dawn on that important day. The period at which this would occur is 1290 B.C.

The second alignment marks Capella rising at the period 1360 B.C. This star could be used either to warn the February sun-rise if that were needed, or it could be used as a clock-star. Attention has already been directed to the doubtful accuracy of the azimuth of this first outlier, and it is noticeable that, as the diagram shows, the alignment passes over stone No. 3. In other cases, it has been observed that one of the members of the circle is frequently placed exactly in the alignment. (For example, at the Keswick Circle (*Proceedings* III., 3, page 77), a stone with a pointed top is exactly in the straight line from the centre of the Circle to the Saddleback-Skiddaw gap.) If, in the lack of knowledge as to the exact position of the first outlier, we *assume* that the line from the centre of the Circle to it would exactly bisect stone No. 3, we may arrive at a more correct value for this alignment. The stone No. 3 is one of the few that is quite upright. It is denuded down to

about 3 feet in height but by taking the mean of the azimuths of the sides of the stone *at the ground*, we may get a fairly good value of the azimuth sought. This turns out to be N.  $23^{\circ} 26' 20''$  E., about  $38'$  difference from that before obtained. The corresponding declination is  $34^{\circ} 43'$ , and this is the declination of Capella at the period 1310 B.C. The last figure is a remarkably strong confirmation of the date 1290 B.C. given by the more accurate and trustworthy alignment I.<sup>1</sup>

The interpretation of alignment III. is doubtful. It might mark the rising of Capella at the period 2150 B.C., the rising of Castor about 1600 B.C., or the rising of Arcturus at the period 0 B.C., each of the stars serving the purpose of "clock-stars." None of these dates are consistent with those furnished by the other alignments, the first two being too early and the last too late to form part of an initial scheme. Further, a star rising  $35^{\circ}$  from the northerly point of the horizon would be of little use as a "clock-star" as it would be invisible through being below the horizon for a very considerable part of each revolution round the pole of the heavens. Two explanations offer themselves:

- (1) Either the present position of the stone is not its original position, and not near its original position; it is to be remembered that it is on a slope and in falling might easily roll some distance;
- (2) Or, the use of the stone was for some religious rather than practical purpose, or perhaps for some practical purpose other than those already suggested. There seems no necessity for supposing that every outlying stone was used for marking alignments to "warning-stars" or "clock-stars."

<sup>1</sup> Hinks: *Astronomy*, p. 8, says:—"At the present time there is a decided tendency to go further than strict prudence would permit, . . . to pretend by measurement and calculation to arrive at the date of the building with all the authority that should attach to the solution of an astronomical problem. We shall do well to receive all such results with caution; they are interesting archaeology, but their astronomy is questionable."

In view of this statement, the above consistency of dates is important.

In a case where no consistent interpretation of this kind can be put upon an alignment, it seems quite reasonable to leave it out as being for a purpose unknown rather than to adhere rigidly to one or other of the possible but improbable meanings that might be assigned to it.

IV.—It will be noticed that at the Girdle Stanes, *two* natural features of the horizon have been made use of to mark alignments—one, to the May sun-rise; the other, to the “warning star” Arcturus. To set up a circle and place outliers to mark the rising and setting of sun and stars is, at any rate in point of design, a comparatively easy feat. To choose the position of the centre of the circle so that some natural feature of the horizon—a hill gap, or a peak—may be used to mark one alignment while stones are set up in suitable places for the other alignments, is a much more difficult task, but still not impossible. Cases of this plan are well known. But to fix the centre of the circle in such a position that *two* natural features may be simultaneously used to mark alignments is a problem requiring much experience and skill for its solution. Expressed geometrically, the second problem is only to find one of the infinite number of points at which the altitude and azimuth of the natural feature reduce to the same required declination. The last problem is to find *one* point, the intersection of two such loci. And the fact that in the theory of the Girdle Stanes, I have required that this one point should be found may be held to weaken the argument by demanding a great deal too much of the intelligence and capacity of the circle-builders of that primeval age. I therefore offer the following remarks in justification of this part of the theory:—

- (a) As I have already said, I planned, before seeing the Circle, to take the azimuth of every outlier and remarkable point on the horizon and then to work out the theory. This is the proper scientific plan.

I found only the two outliers and two hill gaps as recorded. When I proceeded to work out the declinations and find the appropriate meanings, the theory as given unfolded itself without any assistance. To me, however it may appear to others, the perfectly natural way in which this occurred is most convincing.

- (b) A reference to Dr. Morrow's survey of the Keswick Circle\* shows that the possibility of using two natural features was not unknown. There, two features are used but in a peculiar way. The first, the Skiddaw-Saddleback Gap, is connected with the centre of the Circle. The second, the peak Great Mell Fell, is connected with an un-symmetric, specially-constructed rectangle of stones called the chapel. The date finally assigned to the Circle is 1400 B.C., while the date deduced from the latter alignment is 1650 B.C. Dr. Morrow points out, however, that owing to the displacement of the stones of the rectangle this latter estimate is subject to much error. We shall then, with him, discard this date and suppose that the rectangle was set up at any rate not earlier than the rest of the Circle. On accepting this, two further suggestions arise. Either the rectangle was erected after the Circle when it was found that Great Mell Fell was so placed that this slight addition to the Circle would enable the Fell to be used to mark an alignment; or, it may be that it was part of the original plan to use Great Mell Fell with the centre of the Circle, but the design proved faulty and had to be amended by the addition of the rectangle. How near the design was to being a success is evident from the fact that the centre need only have been placed

\* *Proceedings Univ. Durham Phil. Soc.* iii, 3, p. 75.

20 feet away from its present position—at the intersection of the lines drawn from the chapel and from stone No. 1 through the centre as shown in Dr. Morrow's plan, and both natural features would have been available without any chapel. At all events, we have in the 'Keswick Circle' a first approximation to the solution of the problem of using two natural features, and it is not too much to expect an improvement on this a century later, as we have it at the Girdle Stanes.

- (c) The position of the Girdle Stanes sheds a clear light on the question. The rough sketch shows how remarkable is the position of the Circle and points to the fact that this position was not arrived at by mere chance, but was carefully chosen. The ground rises to the north and east, in the former case to an angular altitude of  $3\frac{1}{2}^{\circ}$  at a distance of about 150 yards, in the latter case to an angular altitude of nearly  $9^{\circ}$ , though at a great distance. On the east is the river and to the south is the level rapidly broadening holm. The Circle has been thrust up against the rising ground at the vertex of the rough triangle. Its appearance from the south-east is one of being almost hidden by the over-hanging hillocks, while, approached from the north, it is quite invisible until the observer is within 150 yards. In view of the fact that there is to the south a much wider, clearer space for such a Circle, the position it is now in cannot be accidental. The Holm Craig-Clerk Hill Gap could have been used equally well in a more southerly position. And the only available explanation is that the Circle was thrust north into its chosen place so that at the same time it might be possible to use the Thunderbolt Knowe Gap to mark the May sun-rise.

V.—The conclusion is that the Circle was erected for a two-fold astronomical purpose:—

- (a) To mark the quarters of the agricultural year; and
- (b) To mark the passage of time at night, or more particularly, to warn the approach of dawn on the August and probably the February quarter days so that the astronomer-priests might be ready to greet the sun-rise with their religious celebrations.

The date of erection of the Circle is, with very considerable certainty, 1290 B.C.



# A CASE OF MEGASCOPIIC PSEUDOSTROMATISM IN THE D<sub>5</sub> COAL MEASURES OF NORTHUMBERLAND.

By S. RENNIE HASELHURST, M.Sc., F.G.S.

[Read December 5th, 1911.]

THE SECTION EXPOSED 1. OM TYNEMOUTH TO SEATON SLUICE.

(See sections figs. 1 and 2).

Member.	Phenomena.	Locality.
<b>[HIGH MAIN]</b>		
Grey shales	<i>With pseudostromatism</i>	Black Middens to Spanish Battery.
Red sandstone		
Yellow shales and	<i>With pseudostromatism</i>	St. Mary's Island to Crag Point.
Micaceous sandstone		
<b>GREY SEAM</b>		
Yellow shales	<i>With pseudostromatism and 'cone-in-cone' structure</i>	Sharpness Pt. and Cullercoats.
Red and brown sandstones		
Yellow shales		
Sandstone		Wireless Station to Table Rocks and Kenner's Dene.
<b>YARD SEAM</b>	<i>With fine cuboidal cleat</i>	
Yellow shales	<i>With 'cone-in-cone' structure</i>	
Fireclay		
Brown sandstones	<i>With 'cathedral columns'</i>	Table Rocks.
<b>BENSHAM</b>		
Black shales and sandstones	<i>With cleavage, anticlines and pseudostromatism</i>	Smugglers' Cave.
Red sandstones	<i>With cleavage, anticlines, and pseudostromatism</i>	
* { Table Rocks sandstone	<i>With thrust planes, minor faults, brecciation and pseudostromatism</i>	
Shales		
Musselband		
Shale		
Sandstone		
Shale		
Sandstone		
Shale		
Black and red shales		
<b>LOW MAIN</b>		
Black shales	<i>With thrust planes and squeezing-out of coal seams</i>	
Fireclay		

\* Vide Lebour and Smythe, Q.J.G.S., lxi., p. 533.





Old Pier Works.

SPANISH BATTERY.

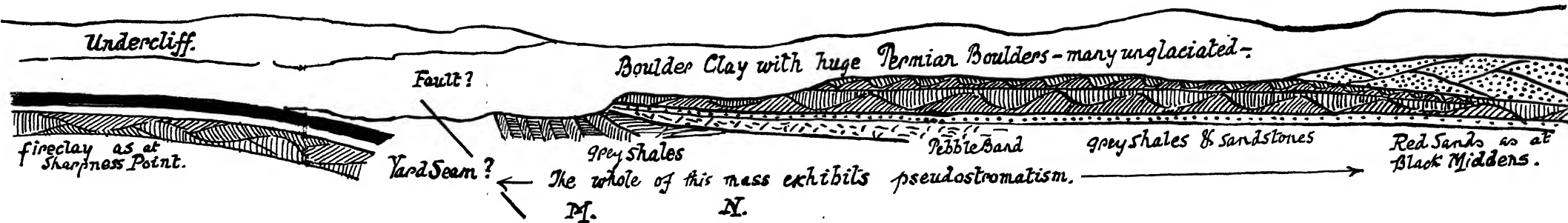


FIG. 1.

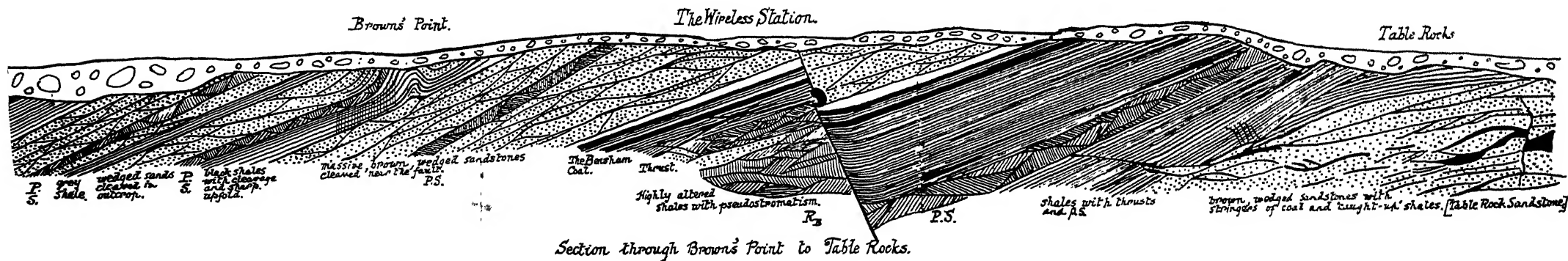


FIG. 2.



*Description of the Section.* (Figs. 1 and 2.)—In the above table only the chief divisions of the series are given and no mention will at present be made of thicknesses. The topographical distribution is shown in the right hand column to simplify the section and to prevent reduplication. The series consists of a variety of rocks varying from soft coals, grey, yellow, and black shales often highly indurated, to mussel bands, fireclays and micaceous and massive sandstones. The sections present many features which are quite new as regards their occurrence in Carboniferous rocks and remind one of features generally ascribed to highly metamorphic rocks. The vein phenomena described in the Permian Yellow Sands<sup>2</sup> are found to be characteristic of the massive brown sands in the vicinity of fault planes, as at Curry's Point, Tynemouth Cliff, and St. Mary's Island.

The grey shales and sandstones of the Black Middens rest on a brecciated bed of shale and are cleaved transversely to the parallel thrust planes intersecting them (see Fig. 3). Similar beds occur below the Bensham, Yard Seam and Grey Seam.

The massive Sandstones at Tynemouth, Brown's Point and St. Mary's Island exhibit large crush veins, the containing walls of which are slickensided and polished in planes pointing N.W. The Brown's Point section (Fig. 2) shows the same sandstones containing huge phacoids and wedges. The finer sandstones, which are always highly micaceous, weather with most beautiful ripple marked surfaces and are *apparently* false-bedded. These sandstones at Brown's Point show a marked anticlinal and the underlying black shales are cleaved in fine parallel planes running west. The whole series in section is characterized by thrust planes passing into reversed faults, wedging out of coal seams as at the Smugglers' Cave, brecciation *in situ*, cleavage and pseudostromatism.

*Description of the Structures.*—Pseudostromatism,<sup>3</sup> false or incipient cleavage, close-joint-cleavage, or strain-slip-cleav-

<sup>2</sup> Haselhurst:—Durham Univ. Phil. Soc., *Trans.*, Vol. 4, pt. i.

<sup>3</sup> Sorby:—*Rep. Brit. Assoc.*, 1885, 836-841.

age,<sup>4</sup> is of frequent occurrence in fine-grained beds. It is really a microscopic phenomenon, and, as the writer could not get a term to describe aptly the features in the above series, the term *megascopic pseudostromatism* is introduced. It sometimes occurs as a parallel system of microscopic faults, sometimes as a system of minute folds. (See Figs. 3 and 4 for megascopic instances.) By means of them rocks exhibit a tendency to split up along definite planes which may be either along the limbs of the folds or along the minute faults. Sorby<sup>5</sup> has shown that these structures represent a transition stage towards a true slaty cleavage. Very frequently, as at the Black Middens, they reproduce in miniature the variety of structures developed in the formation of mountain chains.<sup>6</sup> Thus, overfolds occur in the whole of the section, passing into overthrust faults. Pseudostromatism, as described by Sorby, Bonney, Harker and others, is a frequent result of shearing in finely laminated rocks, and the result is the formation of minute oblique folds with an inclination of about 45 degrees to the planes of lamination (see Fig. 3), "pushed over until at about 30 degrees they pass into little faults, and the faults may be pushed further over until they are lost in the general parallel structure."<sup>7</sup>

This feature of overfolding and cleavage is always developed in the grey and black shales and micaceous sandstones when they occur in sheared and faulted areas. But when the texture of the rock becomes coarser the structure becomes very like false-bedding and ripple-marks, as at Brown's Point and St. Mary's Island. Close inspection of the rock in section (Fig. 4) shows that it bears a striking resemblance to fluxion-structure and in the planes of stratification each individual phacoid bears sinuous flexures, indicating a N.W. shear. The coarser rocks yield in a manner

<sup>4</sup> Bonney :—Q.J.G.S., xlii. *Proc.*, p. 65.

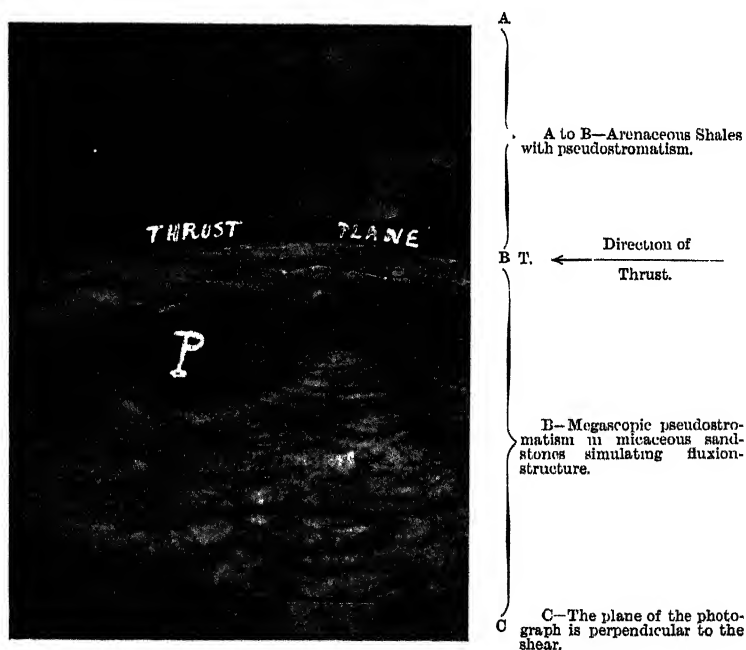
<sup>5</sup> Sorby :—Q.J.G.S., xxxvi. 1880, *Proc.*, p. 72-73.

<sup>6</sup> See specimens in Museum. Dove Marine Laboratory.

<sup>7</sup> Marr :—*Principles of Strat. Geol.*, p. 75.



FIG. 3. —(1) OVER-FOLDED GREY LIMESTONE, (2) PEBBLE BAND AND (3) PHACOIDAL PSEUDOSTROMATISM, (4) WITH THRUST PLANES AT BLACK MIDDENS. [POSITION N IN FIG. 1].



Locality:—Section Fig. 2 at R<sub>B</sub>.





like the Magnesian Limestone of Ryhope and develop phacoids of large dimension, as described by Woolacott.<sup>8</sup> The coals only develop fine cleating. At Sharpness Point the Yard Coal can be taken out in regular centimetre cubes. This also occurs at St. Mary's.

*The Origin of the Structures.*—A reference to the G.S. map 105 N.E. 1" (new series sheet 15) will show the reticulation of the series by a large number of faults (16), the main trend of which is either parallel to the 90 Fathom Dyke or the Brier Dene Fault planes. Particularly should the parallelism of the Brier Dene and Brown's Point faults be noted. The land mass north of Brier Dene has moved N.E., displacing the High Main outcrop nearly two miles, the whole being buttressed against the slip face of the 90 Fathom Dyke. Here, then, is a reduplication of those phenomena described previously.<sup>9</sup> Such a mass, in sinking to the N. by W. and simultaneously moving to the N.E., would affect the beds to the S. so as to produce a shear from the N.W. and a movement over the 90 Fathom Dyke plane in a S. by E. direction.<sup>10</sup> The southward movement would be due to the thrust generated. The conditions of stress and strain set up in such a mass, if we take the evidence of dip which is everywhere inland, would be enormous. It is not to be wondered at, that such an area should be violently disrupted in parts and that those rocks which are less resistant should yield in a manner which clearly establishes the sense and nature of the shear and thrust acting conjointly. This can be shown readily by means of a simple experiment. In Fig. 5 let FF<sub>1</sub> represent the resistance of the 90 Fathom Dyke Fault plane, let the boards of the book be the planes of stratification and let PQ be a series of coarse sandstones resting upon micaceous sandstones or shales, let the clamp represent the thrust acting from the north towards the south. The resistance of

<sup>8</sup> Woolacott:—"The stratigraphy and tectonics of the Permian of Durham, (Northern area)." Abstract in Q.J.G.S., Vol. 67, p. 312.

<sup>9</sup> Haselhurst:—*op. jam. cit.*

<sup>10</sup> Haselhurst, *op. jam. cit.*

the lower beds is obviously directed towards the north. The laminæ of the lower beds are flexured with the apices of the folds directed towards the south. The overfolding, if prolonged, would rupture along XY and give a reversed fault with parallel cleavages, in the shales and vein masses, slickensided by the N.W. shear in the overlying sandstones. If the shales alternate with more resisting material, they will rupture rather than fold and the hard bands will plough into the shales if below them. Field illustrations of this principle are numerous in the section. What might be termed the inter-fault areas (*i.e.*, St. Mary's to Crag Point) indicate that, in the main, the pseudostromatism developed in that gently undulating series points to a gentle pressure flow along the less resisting strata, always shearing from the N.W., and attaining its grander proportions with disruption, folding, cleavage and tilting in the immediate proximity to the major fault planes.

The writer wishes to express his indebtedness to Drs. Woolacott and Smythe for their criticisms and help and to Mr. Rang for Fig. 3.

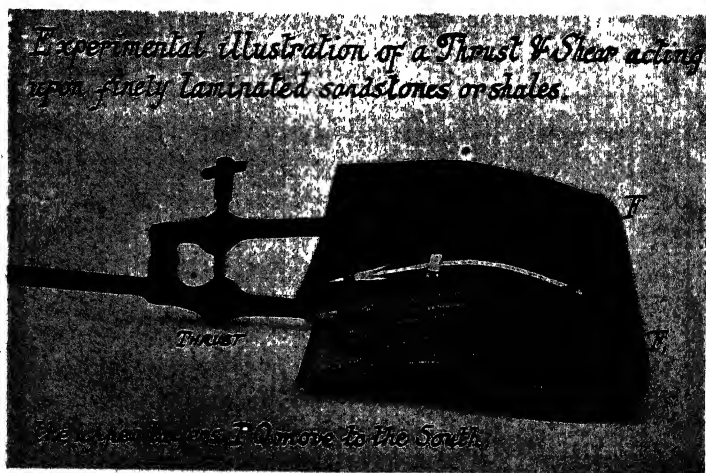


FIG. 5.

ON THE BEST USE OF A CONDENSER WHEN USED  
AS A SHUNT TO A TELEPHONE IN WIRELESS  
TELEGRAPHY.

By H. SMITH B.Sc.

[Read December 7th, 1911.]

In practically all systems of Wireless Telegraphy the telephone receiver has superseded all other forms of reception and it is therefore a matter of importance to examine the conditions under which the telephone is employed, in order to determine the most advantageous relations between the constants of the various parts of the circuit.

It has been found for the telephones used in practice that the best results are obtained when the telephone is shunted with a capacity. The best value of the capacity depends among other things on the telephone, and the practical rule has been that the greater the resistance of the telephone the less the value of the capacity to give the loudest sound.

It is sometimes stated that the function of the capacity is to form an easy path to the oscillations past the telephone whose inductance when introduced into the oscillating circuit would otherwise seriously enfeeble the current strength. That this explanation is insufficient is clear from the fact that there is an optimum value of the capacity. It was with the object of affording an explanation of this phenomenon that the following work was undertaken.

Fig. 1 shows a very usual method for coupling the receiving circuit with the antenna. The adjustable condenser  $C_1$ , made use of only under certain circumstances, allows of tuning in the receiving circuit and is generally very much smaller than the block condenser,  $C$ , used as a shunt to the telephone,  $T$ . If  $C$  is increased while the messages are being received the intensity in the telephone increases at

first, followed by a deadening and lowering of the note due, one might imagine to the suppression of the higher harmonics. As the condenser  $C$  and the inductance of the telephone  $T$  form an oscillating circuit, it is reasonable to expect resonance with some of the harmonics. If this be so, the best value of the capacity  $C$  will be when the telephone circuit is in resonance with the more pronounced of these harmonics. Moreover, the addition of an inductionless resistance, if of sufficient value, to the telephone circuit

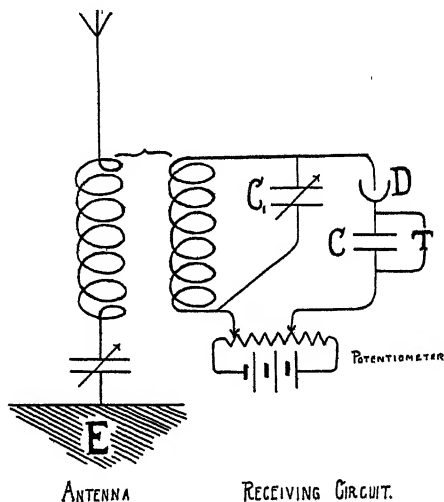


FIG 1

should effectively prevent all resonance and no rise in intensity in the telephone would be observed. Experimenting with the arrangement in Fig. 2, I found this actually to be the case; indeed, with one telephone I tested, whose resistance was large compared with its inductance (2,000 ohms and .02 henry respectively), there was a continuous fall off in intensity from the moment condenser  $C$  was put across it without any further addition of resistance.

The current through the telephone is, of course, inter-

mittent, occurring every time the detector D is traversed by oscillations picked up from the antenna. We may, however, regard it as an alternating current whose frequency is that of the break in the primary current at the sending station, and which has superposed on it a direct current, and contains in it also a large number of harmonics.

The following arrangement was adopted as sufficiently well reproducing the condition of things in the receiving circuit.

L represents the inductance of the receiving circuit. The seat of the E.M.F., as before, is in the circuit LC but is produced by coupling with an alternating current instead of being taken from a potentiometer.

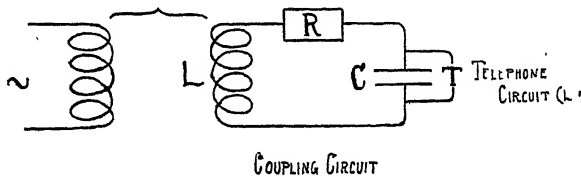


FIG 2

With such an arrangement as this the current due to any particular harmonic through the telephone is a maximum when

$$C = \frac{L}{R^2 + \omega^2 L^2} + \frac{L_1}{R_1^2 + \omega^2 L_1^2}$$

Where L and R are the inductance and resistance of the coupling circuit LC,  $L_1$  and  $R_1$  the inductance and resistance of telephone circuit consisting of the telephone and the condenser C, and  $\omega = 2\pi \times$  frequency of the harmonic.<sup>1</sup>

When  $R_1$  is very large and R small, very beautiful resonance in the coupling circuit with the harmonics in the alternating supply is obtained. The intensity of the sound in the telephone is a series of maxima, each maximum giving a

<sup>1</sup> 'A Method for the Detection of Harmonics.' *Electrician*, June 2nd, 1911.

different note whose frequency is the same as the harmonic. In the case of wireless telegraphy the resistance  $R$  is in general great due to the detector; and from the symmetry of the expression given for the value of  $C$ , if  $R_1$  were small this time we should expect to have the same phenomena in the telephone.  $R_1$  however is not small, and instead of hearing several notes at different maxima, the intensity rises to one maximum only, not very sharply defined.

With three different telephones the following results were obtained :—

TABLE I.

Telephone's Resistance.	Telephone's Inductance.	Value of Capacity to Produce Maximum.	Frequency of Telephone Circuit.
3.75 ohms.	4 millihenries.	4.5 microfarads.	1190
130 „	48 „	.3 „	1340
157 „	100 „	.2 „	1130

We see from this that when the maximum occurs the frequency of the telephone circuit is very approximately the same for very different telephones. No very good agreement can be expected as not only is the inductance of a telephone difficult to measure accurately, owing to its resistance, but the optimum value of the capacity is not very easy to note. The constants of the coupling circuit LC were  $L=158$  millihenries and  $R=4,000$  ohms.

To study better the effects of resonance in the telephone circuit, the following arrangement was adopted :—

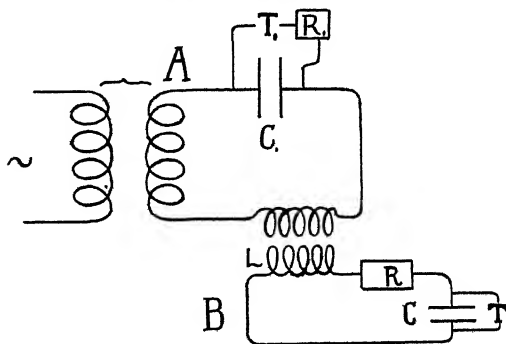


FIG 3

Circuit A is brought into resonance with any desired harmonic by varying  $C_1$  and listening in the telephone  $T_1$  ( $R_1$  must be large—say 10,000 ohms) till the corresponding note is a maximum.<sup>1</sup> Circuit B is now coupled with A, and C varied till the harmonic gives a maximum in the telephone T. In this way the following results were obtained:—

TABLE 2.

Harmonic.	Frequency of Harmonic.	Telephone's (T)		Value of Capacity to Give Maximum.	Frequency of Telephone Circuit.
		Resistance.	Inductance.		
3rd	240	157	100 mlh.	1 mfd. (approx.)	437
15th	1200	3.75	4 „	4.5 mfd.	1190
		130	48 „	.35 „	1230
		157	100 „	.2 „	1130

The discrepancy between the frequency of the harmonic and that of the telephone circuit (calculated by taking into account its resistance which is effective in low frequencies) in the first case is very great. It is due partly to the fact that it was very difficult to decide when the maximum occurred, but chiefly to the existence of the higher harmonics, as the 5th and 7th, which were still quite strong. To separate mentally the effect of each note was impossible.

In the case of the other telephones, I was unable to determine the optimum capacity at all, the change in intensity was so imperceptible, but for the small inductance telephone it was certainly greater than 12 microfarads. With the 15th harmonic it was different, as it was very much more powerful than any of its neighbours when separated in the way given above, and fair agreement between its frequency and that of the telephone circuit was obtained.

It would appear, then, that when a telephone is shunted with a condenser, the maximum intensity in the sound which occurs is due to resonance in the telephone circuit with the various harmonics, the maximum being in reality a compromise of several maxima due to several harmonics. In the case worked out above, it occurred in the region of the maximum produced by the 15th harmonic, which was a particularly prominent one.



Applying these results to the case of the telephone used as a receiver in wireless telegraphy, we see that the value of the capacity used as a shunt to the telephone, which produces the maximum intensity in the telephone, is not independent of the break in the primary current at the sending station: that in the general case, where circuits in parallel with the telephone have a large resistance, this maximum is due to resonance in the telephone circuit alone; that the "harmonics" in the break, and not the frequency of the break itself, may be the most important factor in determining the value of the capacity to produce the best effect for any one telephone.

In conclusion, I wish to thank Prof. Stroud for the kind interest shown in these experiments and for placing at my disposal the necessary apparatus. I wish also to acknowledge my indebtedness to Mr. Morris-Airey, who proposed to me the problem and removed many of the difficulties that arose.

## A PRELIMINARY NOTE ON THE UNIAXIAL AUGITES OF THE NORTH OF ENGLAND IGNEOUS DYKES.

By MARY K. HESLOP, M.Sc.

[Read December 11th, 1911.]

The microscopic investigation of these crystals in the north country rocks was first suggested to me by Dr. Flett, and through the kindness of Dr. Teall, Director of H.M. Geological Survey, I was permitted to work at the Jermyn Street Museum; thus having the privilege of the expert help and advice of Dr. Flett—then Petrologist to the Survey—and the use of such instruments, specimens and slides as enabled me to carry on the work in as favourable circumstances as could be desired.

The somewhat curious appearance—dark colour and

decided pleochroism—of certain large porphyritic augites of the Cleveland Dyke attracted my attention some time ago. One cross-section in particular was remarkable in that it seemed, at first sight, to be isotropic; moreover it yielded what appeared to be a uniaxial interference figure in convergent polarized light. On rotation of the stage, however, the black cross divided into distinctly separate hyperbolæ, so that it seemed probable that the crystal was a biaxial one with an unusually small optic-axial angle.

Further research revealed the existence of a large number of crystals having abnormal interference figures, and wherever possible the angle  $2E$  (represented by the distance between the darkest points of the hyperbolæ) was measured. These readings gave a majority of axial angles between  $13^\circ$  and  $22^\circ$ , while some increased to  $30^\circ$ ,  $50^\circ$ , and  $70^\circ$ , thus becoming more or less normal. Some figures showed no separation into hyperbolæ and were, to all intents and purposes, uniaxial. We recognise, therefore, a great range of axial angles—from  $0^\circ$  to  $70^\circ$ —in these augites.

Uniaxial augites have been recorded by Wahl in the Whin Sill at Belford, and his classic paper deals with many examples from other—especially foreign—localities. The discovery of crystals in the Cleveland Dyke similar to those described by Wahl, led me to make an exhaustive search—which is still in progress—through all available slides of the North of England igneous dykes, including those in the official survey collection and in Dr. Teall's private collection.<sup>1</sup>

The results of this investigation up to the present time may be briefly stated thus—

I. In the Whin Sill and older (Carboniferous) Dykes, the uniaxial crystals are small twinned individuals which are often pierced by felspar laths (and

<sup>1</sup> Through the great kindness of Dr. Teall and Dr. Flett, I am quite at liberty to quote and use the results of these investigations.—M.K.H.

therefore belong to a comparatively late period of crystallization). They are not pleochroic and do not differ in any external feature from the ordinary ground-mass augites. Sometimes they show that the optic axial plane is parallel to the twinning plane (100) instead of being perpendicular to it.

II. In the Cleveland Dyke—which is usually supposed to be of Tertiary age—the uniaxial augites are for the most part large and porphyritic, clearly belonging to an earlier period of crystallization. These are greenish-brown in colour and distinctly pleochroic; but no definitely twinned (normal) crystal has yet been found, so that it is uncertain whether the optic axial plane is parallel to (100) or (010).

Wahl is of opinion that the optic axial angle decreases with a change in chemical composition, until the interference figure is uniaxial, then the axes (he supposes) open out in a direction at right angles to their former position, and continue to separate until the axial angle is as large as before. He has also noticed an increase in the size of the angle towards the outer limits of some crystals. I could find no such variation in my specimens.

It is hoped that this subject may be more comprehensively treated in a future publication, and that full reference may then be made to the literature dealing with these abnormal uniaxial monoclinic crystals.

# Financial Report for Session 1910-11.

## General Revenue Account.

INCOME.		EXPENDITURE.	
	£ s. d.		£ s. d.
To Transfer from Reserve Fund...	...	By Deficit brought forward	16 16 2
" Bank Interest ...	...	" Expenses of Meetings	2 17 10
" Sale of Proceedings	...	" Stationery	3 18 6
" Sale of Memoir 1	...	" Postage	6 14 7
" Grant from Armstrong College for Society's	...	" Assistant Treasurer and Clerical	3 4 0
Exchanges	...	" Cost of Authors' Reprints	4 13 6
" Sale of Authors' Reprints	...	" Printing Proceedings:—	
" 194 Annual Subscriptions:—		Vol. IV., Pt. 1	£16 17 6
10 for 1909-1910	£ 2 10 0	Vol. IV., Pt. 2	17 6 4
116 at 10/-	73 15 0		
63 at 5/-	1 0 0	" Balance in Bank	...
3 for 1911-12	0 15 0		...
2 for 1912-13	...		...
	78 0 0		33 13 10
			36 2 4
			£108 0 9

## Reserve Fund.

	£ s. d.		£ s. d.
Donations received	...	Transferred to Revenue Account	16 16 2
	...	Balance in Bank	40 9 4
	...		...
	...		...
	...		£57 5 6

T. H. HAYLOCK,  
Hon. Treasurer.

Audited and found correct,  
C. M. JESSOP.

October 17th, 1911.



# UNIVERSITY OF DURHAM PHILOSOPHICAL SOCIETY.

## THE STABILITY OF A FLOATING TRIANGULAR PRISM.

BY F. H. ALEXANDER.

[Read 13th March, 1911.]

In studying the stability of floating bodies it may often be necessary to use graphical or other approximate methods: but it is of interest to illustrate the general principles by cases which are capable of exact solution. In the following notes the body has the form of a triangular prism; the prism is assumed to be of constant equiangular section throughout its length, and of uniform density. Rotation is considered about one axis only, namely, that which passes through the centre of total volume and perpendicular to the triangular sections. The length of the prism is omitted from all expressions for statical linear values in a transverse plane.

Fig. 1 shows the position which is taken as origin for inclinations. The positions shown in Figs. 1 and 2 alternate at angular intervals of  $60^\circ$ , and this interval, therefore, forms the range of inclinations to be considered.

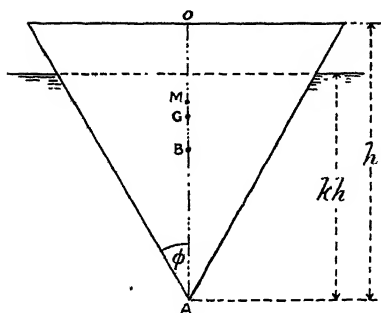
If  $h$  and  $kh$  have the meanings indicated in Fig. 1, then the specific gravity of the prism relative to that of the fluid in which it floats is expressed by  $k^2$ .

In all the figures G represents the centre of volume of the prism, B the centre of volume of displaced fluid, M the meta-centre; and the transverse plane shown is that which contains these three points.

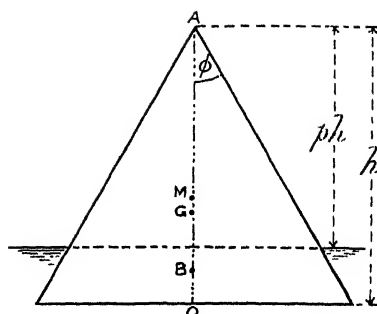
(1) In the position shown in Fig. 1:—

$$\begin{aligned} GM &= AB + BM - AG \\ &= \frac{2}{3} kh + \frac{\frac{k^3 h^3}{k^2 h^2} \tan^3 \phi}{\tan \phi} - \frac{2}{3} h \quad . \quad . \quad . \quad . \quad (1) \end{aligned}$$

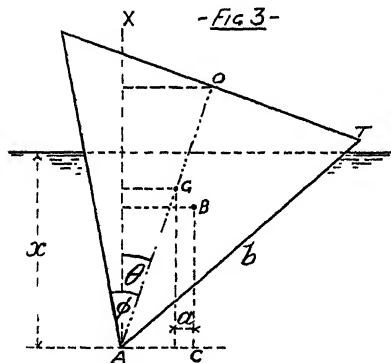
-Fig 1-



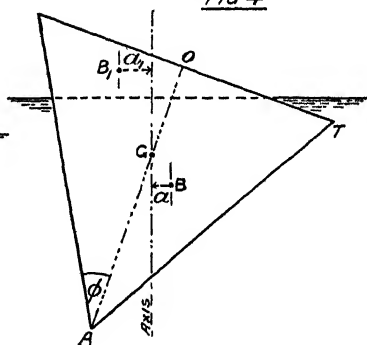
-Fig 2-



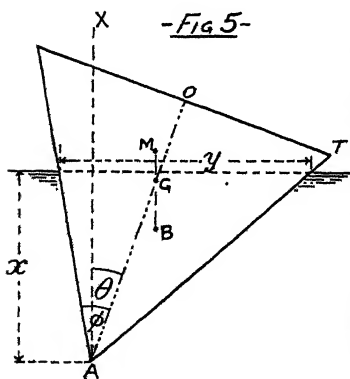
-Fig 3-



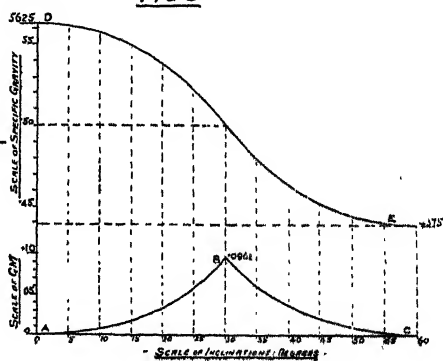
-Fig 4-



-Fig 5-



-Fig 6-



Solving this,  $AM = \frac{8}{9}kh$ , and  $GM$  is negative when  $k$  is less than  $\frac{3}{4}$ ; so that the specific gravity of the prism must be greater than  $\frac{9}{16}$  in order that it may be in stable equilibrium in this position.

(2) In the position shown in Fig. 2:—

$GM = AG - (AB - BM)$ . On reduction this gives

$$GM = \frac{2}{3}h - \frac{6 - 8p^3}{9 - 9p^2} \cdot h \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$GM$  is positive when  $p$  is greater than  $\frac{3}{4}$ ; therefore the specific gravity must be less than  $\frac{7}{16}$ , in order that the prism may be in stable equilibrium in this position.

$AM = (6 - 8p^3)h / (9 - 9p^2)$ . Differentiating with respect to  $p$ , and equating to zero,  $AM$  is a maximum when the specific gravity is about 0.689.

(3) In a position inclined at an angle  $\theta$ , as shown in Fig. 3:—

The moment tending to restore the prism to the position shown in Fig. 1, is the product of the weight of displaced fluid into the distance  $a$ .

If  $x$  is depth of immersion in the given position and  $kh$  that of the same immersed volume in the position of Fig. 1, then since the immersed areas are equal,

$$\frac{1}{2}x^2\{\tan(\phi + \theta) + \tan(\phi - \theta)\} = k^2h^2 \tan \phi.$$

Putting value of  $\tan \phi$ , and simplifying—

$$x = kh \cdot \cos \theta \sqrt{1 - \frac{1}{3} \tan^2 \theta} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The moment of the immersed section about the axis  $AX$  is—

$$\frac{1}{6}x^3\{\tan^2(\phi + \theta) - \tan^2(\phi - \theta)\}.$$

Dividing this by the area of the section—

$$AC = \frac{1}{3}x\{\tan(\phi + \theta) - \tan(\phi - \theta)\} \quad . \quad . \quad . \quad (4)$$

Subtracting the value of  $AG \sin \theta$ ; substituting the value of  $x$  from (3); and simplifying—

$$a = \frac{1}{6}h \sin \theta \{8k(1 - \frac{1}{3} \tan^2 \theta) - \frac{1}{3} - 6\} \quad . \quad . \quad . \quad (5)$$

This equation for  $a$  applies up to the inclination  $\theta_c$ , at which an edge (such as  $T$  in Fig. 3) comes to the fluid



surface. At greater inclinations the shape of the immersed section is quadrilateral, but that of the emerged section is triangular, as is shown in Fig. 4. The following principle may then be applied:—

The sum of the moments of the emerged and the immersed parts of the prism is zero about an axis through the centre of total volume. The specific gravity of the emerged part is obviously  $1-k^2$ . If  $B_1$  is the centre of volume of the emerged part (Fig. 4) then

$$(1-k^2)a_1 = k^2 \cdot a.$$

Now  $a_1$  may be determined by (5) if  $\frac{\pi}{3} - \theta$  is put instead of  $\theta$  and  $\sqrt{1-k^2}$  instead of  $k$ . Thus for inclinations greater than  $\theta_c$

$$a = \frac{1-k^2}{k^2} \times \frac{h \sin\left(\frac{\pi}{3} - \theta\right)}{9} \left\{ \frac{8\sqrt{1-k^2}}{\sqrt{1-\frac{1}{3}\tan^2\left(\frac{\pi}{3} - \theta\right)}} - 6 \right\} \quad (6)$$

This principle of “complementary volumes” is used in similar manner for the other functions required in later expressions.

(4) To determine the angle  $\theta_c$  at which the above change of procedure is necessary, it is seen (Fig. 3) that when T reaches the fluid surface—

$$x = kh \cos \theta_c \sqrt{1 - \frac{1}{3} \tan^2 \theta_c}$$

$$\text{and } x = b \cos (\phi + \theta_c)$$

Putting  $h = b \cos \phi$ , inserting the value of  $\cos \phi$ , and equating the above values of  $x$

$$\tan \theta_c = \sqrt{3}(1-k^2)/(1+k^2) \quad . \quad . \quad . \quad . \quad (7)$$

(5) It is now possible to determine the inclination taken by the prism for positions of equilibrium when the specific gravity lies between  $\frac{1}{16}$  and  $\frac{9}{16}$ .

From equation (4), for equilibrium  $a = c$ , and if  $\sin \theta$  is not zero,

$$\tan \theta = \sqrt{\frac{1}{3}(9-16k^2)} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Using the complementary method when  $h^2$  lies between  $\frac{1}{2}$  and  $\frac{7}{16}$

$$\tan\left(\frac{\pi}{3} - \theta\right) = \sqrt{\frac{1}{3}(16h^2 - 7)} \quad . \quad . \quad . \quad . \quad (9)$$

In order to determine if the equilibrium is stable at these inclinations it is necessary to know that M is not below G. In Fig. 5—

$$GM = BM - BG = \frac{y^3}{6x^2} - \frac{2}{3}(h \cos \theta - x).$$

Putting  $y = x\{\tan(\phi + \theta) + \tan(\phi - \theta)\}$

$$BM = \frac{2}{3}x(\cos^2 \theta - \frac{1}{3} \sin^2 \theta)^{-2} \quad . \quad . \quad . \quad . \quad (10)$$

and substituting value of  $x$  from (3)

$$GM = \frac{2}{3}kh \cos \theta \left[ \left(1 - \frac{1}{3} \tan^2 \theta\right)^{\frac{1}{2}} \{(\cos^2 \theta - \frac{1}{3} \sin^2 \theta)^{-2} + 3\} - \frac{2}{3}k^{-1} \right] \quad . \quad . \quad . \quad (11)$$

Solutions show that the equilibrium is stable in all the positions. Fig. 6 shows the results in graphic form. For given specific gravity on DE, the angle of equilibrium is on AC, and the corresponding metacentric height in terms of  $h$  on ABC.

(6) The locus of the centres of constant immersed volume for successive inclinations is called the "curve of buoyancy." Its co-ordinates are AC and BC (Fig. 3). AC is given by (4) and  $BC = \frac{2}{3}x$ . The radii of curvature of this locus are the values of BM given by (10).

(7) The locus of centres of area of surface waterplanes which cut off constant immersed volume at successive inclinations is called the "curve of flotation."

It may be shown that the radius of curvature  $r$  of this locus is given by—

$$r = \frac{1}{3}x(\cos^2 \theta - \frac{1}{3} \sin^2 \theta)^{-2} \quad . \quad . \quad . \quad . \quad (12)$$

When  $\theta = 0$  the initial radius is obviously  $\frac{1}{3}kh$ .

At inclinations greater than  $\theta_e$ ,  $r$  becomes negative in direction.

(8) Work is performed in changing the inclination of the prism. This work may be determined by either of two methods, namely:—

(a) The product of the weight ( $W$ ) of displaced fluid into the change of vertical separation of B and G due to change of inclination.

For example when  $\theta = 0$  (Fig. 1) the vertical separation of B and G is  $\frac{2}{3}(h - kh)$ ; in an inclined position (fig. 3) the separation is  $\frac{2}{3}(h \cos \theta - x)$ . Hence putting the value of  $x$  in (3), the change of separation ( $\lambda$ ) is

$$\lambda = \frac{2}{3}h\{\cos \theta - 1 + k(1 - \cos \theta(1 - \frac{1}{8}\tan^2 \theta)^{\frac{1}{2}})\} \quad (13)$$

and the work done is  $W\lambda$ .

(b) The integral of the statical righting moments with respect to inclination, within the limits of change of inclination.

In the example given above the work done is thus  $W \int_0^\theta a \cdot d\theta$ . and putting  $a$  as given by (5) this is

$$\frac{1}{8}Wh \int_0^\theta \left\{ \frac{8k \sin \theta}{\sqrt{1 - \frac{1}{8}\tan^2 \theta}} - 6 \sin \theta \right\} d\theta.$$

The evaluation of the integral gives  $W\lambda$ , as in (13). As written, the integral applies to changes of inclination within the limits of  $\theta_0$  and  $\theta_e$ . For inclinations within the limits  $\theta_e$  and  $\theta = \frac{\pi}{3}$  the integral must be based on (6) instead of on (5).

## SOME OBSERVATIONS ON THE EFFECT OF SOIL AERATION ON PLANT GROWTH.

By C. HUNTER, B.Sc.

[Read March 12, 1912.]

Dehérain and Vesque in 1876<sup>1</sup> determined the amount of carbon dioxide which was given off by roots in a chamber containing damp air, and clearly proved that carbon dioxide is one of the products of the katabolic processes in the living root. When this gas is present in excess it has a pernicious effect upon the growth of plants, the roots suffer from poor oxygenation and organic acids are excreted instead of carbon dioxide and water. Stoklasa and Ernst<sup>2</sup> have identified traces of acetic and formic acids which have been excreted by the roots of corn and barley which have been insufficiently oxygenated.

In this communication an account is given of some preliminary experiments which were designed to investigate the effects of different degrees of soil aeration on plants. The method adopted in the first type of experiment was to mix carefully some soil in order to render its composition as uniform as possible. The soil was then placed in four series of 5-inch pots and arranged so as to give five degrees of texture:—

Pot No. 1.	Soil in small lumps, loose.
Pot No. 2.	Soil fine, loose.
Pot No. 3.	„ „ firm below with a loose surface.
Pot No. 4.	„ „ firm.
Pot No. 5.	„ „ hard.

<sup>1</sup> *Ann. d. Sci. nat.*, Sér. 6, t. vii.

<sup>2</sup> *Beiträge zur Lösung der Frage der chemischen Natur des Wurzelsekretes.* Jahrb. f. wiss. Bot. 46 (1908).

Carefully selected seeds of *Helianthus*, *Pisum sativum*, *Triticum*, and *Lepidium sativum* were planted in these pots and every care was taken to eliminate disturbing factors. The amount and the circulation of the air were the only variable factors and any differences in the growth of the plants must be largely attributed to their influence. Photographs were employed to make a record of the differences in the amount of plant growth. That these differences were not due to chance was proved by repeating the experiment with different kinds of soil. Garden loam, a mixture of loam and sand, loam containing fibre, and the soil obtained by rubbing together pieces of turf all gave similar results. In every case the seeds in the pot containing the hard soil did not germinate so well as those in pots 1-4. This effect was most marked in the case of the cress and the peas, neither of which were able to germinate (see Fig. 1). It was found to be necessary to examine the root systems of the plants and to note the effects of the varying conditions of the soil upon them. The roots of the wheat in Pot No. 1 (see Fig. 2) were the longest, but very few particles of soil adhered to them. The root systems in No. 3 were shorter but were densely covered with soil particles. The loose soil in No. 2 gave intermediate results between No. 1 and No. 3. The roots were longer than those in No. 3, but they had soil adhering to them only in patches.

The roots in No. 4 were not so well developed as those in No. 3, but they were well covered with soil. The plants in No. 5 were small and the roots were unable to leave the surface. Somewhat similar results were obtained with the peas. The plants which were grown in the loose fine soil appeared to be the strongest, their leaves were the largest, and their root systems were the best developed of the series (see Fig. 3).

Estimations of the relative water content of the soil from the different pots did not show any appreciable relation to these results, so it cannot be argued that they were due

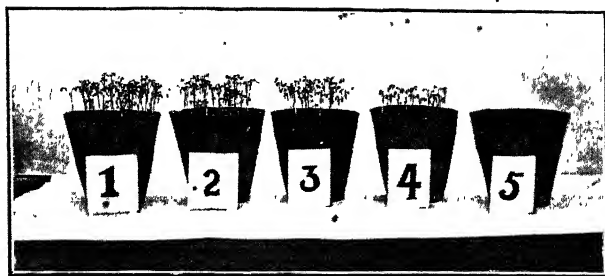


FIG. 1. SEEDLINGS OF *LEPIDIUM SATIVUM*.

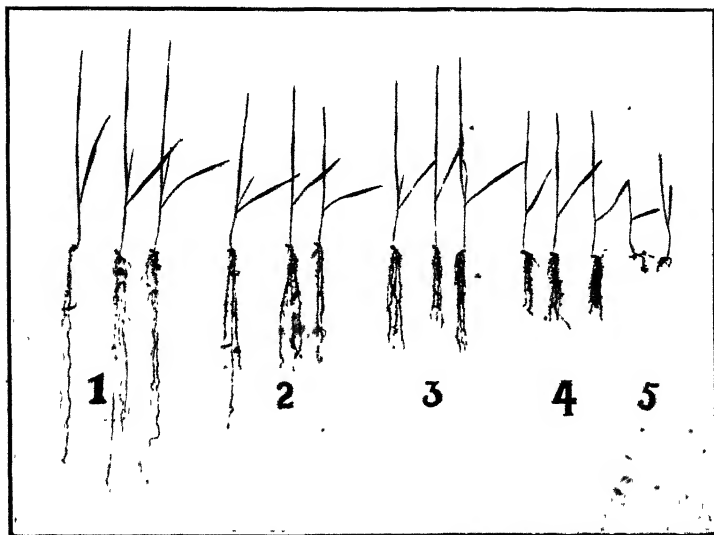


FIG. 2. WHEAT PLANTS



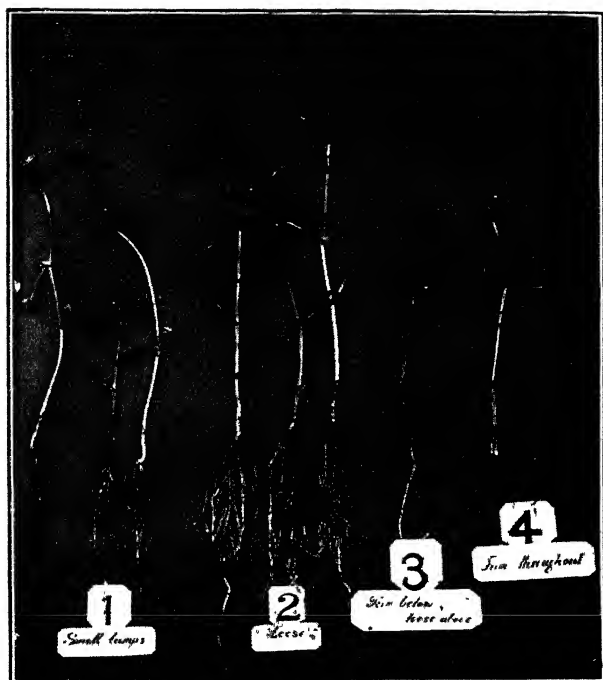


FIG 3. PISUM SATIVUM





to the varying amounts of water in the soils. A few preliminary estimations of the numbers of bacteria present in the different conditions of the soil have been made but no definite relations between this possible factor and the amount of plant growth could be established. The differences in the amount of plant growth must be attributed to the amount and movement of the air present in the soil. Experiments were made in order to obtain some comparative results dealing with the resistances of soils to air movements. It was found that columns of soil offered different resistances to this artificial air current in accordance with their textures.

Kind of Soil:—Loam mixed with fibre.

Description of Soil.	Height.	Resistance Offered.
1. Small lumps, loose .. ..	35 cms.	1 unit.
2. Fine, loose ... ..	35 cms.	2 units.
3. Fine, firm below with loose surface	{ 5 cms., loose. 30 cms., firm.	17 „
4. Fine, firm throughout ... ..	35 cms.	42 „
5. Fine, hard throughout ... ..	35 cms.	310 „

When these figures are compared with the results of the experiments dealing with the growth of plants in these different kinds of soil they seem to point to an optimum amount of circulation of air in the soil for different kinds of plants. Thus for wheat the optimum condition is when the soil offers a resistance of about 17 units according to our method of reckoning and at the stages at which the plants were examined.

The effect of producing artificial air currents in the soil was next tried with young plants of *Pisum sativum*. The soil was made uniform in each of five large glazed pots and 15 litres of air were drawn through the soil in one of these pots each day for three weeks. The seedlings chosen were badly developed, their stems were weak and the leaves curled. In two or three days those that were subjected to these arti-

ficial air currents became more robust, the stems became stronger, the leaves grew rapidly and became much larger than those of the control plants.

As a result of the various experiments which have been carried out with the object of investigating the connection between soil aeration and plant growth, it has been found that—

The circulation of the air in the soil affects the development of the root system and through that the development of the sub-aerial portions of a plant.

The production of artificial air currents in the soil appears to be beneficial to plant growth. This point is at present undergoing further investigation.

These experiments were undertaken at the suggestion of Professor Potter, to whom I wish to express my thanks for the kind interest he has shown in the work. I also wish to acknowledge my indebtedness to Mr. Mangham for his help and advice.

THE INVESTIGATION OF THE CHEMICAL REACTIONS  
TAKING PLACE AT THE CATHODE AND ANODE  
DURING THE ELECTROLYSIS OF SIMPLE SALT  
SOLUTIONS.

BY J. HAMILTON PATERSON, D.Sc.

[Read February 15th, 1912.]

PART I.

Modern research in the phenomena attending electro deposition has been for the most part carried out with a view to producing accurate processes for the electro analysis of metallic substances.

In order to obtain smooth and adherent deposits of the pure metal numerous empirical processes have been described, the majority of them depending on the use of complex salts of the metal in question for their success.

When simple salts of the metal are used, considerable difficulty is often experienced in obtaining pure metallic deposits. Spongy non-adherent precipitates are produced which contain other elements (notably hydrogen and oxygen) beside the metal itself.

A short tabulated list of the results obtained during a series of preliminary experiments, is given below. These experiments were done with a view to comparing the results obtained by the electrolytic deposition of simple salt solutions with those of the complex salt solutions usually recommended for electro analysis, under the same conditions. The apparatus used in these experiments was constructed as follows (Fig. 1):—

Two platinum discs (E and E<sup>1</sup>), 1½ inches in diameter, were used as electrodes. Attached to these were thick copper

wires ending in screw-down terminals threaded on a glass rod G, which stretched across the top of a wide beaker of about 250 c.c. capacity. The backs of the electrodes and the copper leads were covered with a coating of glass enamel. By sliding the electrodes along the glass rod the distance between them could be increased or decreased by known amounts and thus different conditions of current density produced in the same solution. The contents of the beaker were kept gently stirred during the actual experiments by means of a Witt stirrer S. The source of current was a battery of four accumulators and included in the circuit

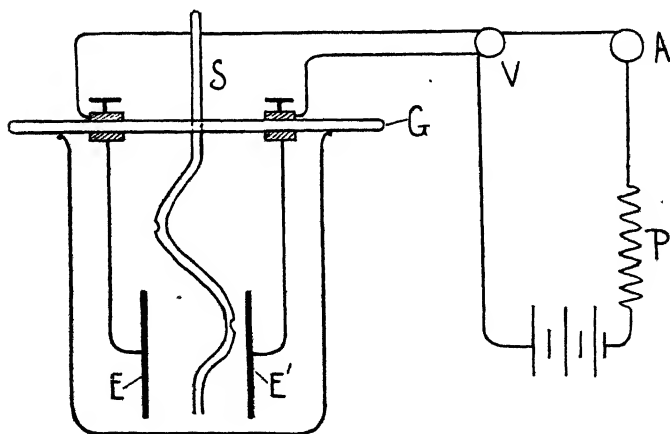


FIGURE 1.

were a delicate amperemeter A, a voltmeter V and a rheostat P. The surfaces of the electrodes were examined from time to time with a powerful telescope during the course of the experiments. Polished surfaces were always used. The different temperatures noted were all obtained by direct heating of the beaker.

In those cases where the directions of a previous experimenter have been followed, his name is given in the last column.

(Three per cent. solutions of the crystalline salts named were used.)

TABLE A.

Metal	Salt Used.	Substances Added.	Volts.	Current Density.	Temp.	Cathode Reaction.	Anode Reaction.	Experimenter whose directions were followed.
Fe"	FeSO <sub>4</sub>	.....	7.0	1.20	25°C.	Fe (spongy) ..	Fe(OH) <sub>3</sub> ..	.....
Fe*	FeSO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> molec. proportion ..	4.2	1.3	50°C.	Fe (dull) ..	.....	.....
Fe"	FeSO <sub>4</sub>	Excess of (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ..	3.8	1.2	50°C.	Fe ..	.....	.....
Fe"	Fe(NO <sub>3</sub> ) <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> and nitric acid 1% ..	3.0	1.4	50°C.	Fe (dull) ..	Fe(OH) <sub>3</sub> ..	.....
Fe"	FeCl <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> in excess ..	3.5	1.2	50°C.	Fe ..	.....	.....
Ni	NiSO <sub>4</sub>	.....	7.5	.64	15°C.	Ni ..	.....	.....
Ni*	NiSO <sub>4</sub>	.....	7.2	1.35	15°C.	Ni & Ni(OH) <sub>2</sub> ..	.....	.....
Ni	NiSO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> and excess of NH <sub>3</sub> ..	3.0	1.0	25°C.	Ni ..	.....	.....
Ni	NiSO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> in molec. proportion ..	3.5	1.3	25°C.	Ni ..	NiO <sub>2</sub> & Ni <sub>2</sub> O <sub>3</sub> NiO <sub>2</sub> & Ni <sub>2</sub> O <sub>3</sub>	.....
Ni	NiSO <sub>4</sub>	HNO <sub>3</sub> 1% ..	3.0	1.3	25°C.	.....	.....	.....
Co	CoCl <sub>2</sub>	.....	7.5	.75	17°C.	Co (dark) ..	.....	.....
Co*	CoCl <sub>2</sub>	.....	7.5	1.2	20°C.	Co & Co(OH) <sub>2</sub> ..	Co <sub>2</sub> O <sub>3</sub> ..	.....
Co	Co(NO <sub>3</sub> ) <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> in molec. proportion ..	4.0	1.3	25°C.	Co ..	.....	.....
Co	CoCl <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> in excess ..	3.8	1.6	25°C.	Co ..	.....	.....
Cd	Cd(NO <sub>3</sub> ) <sub>2</sub>	.....	3.0	.65	50°C.	Cd (dark) ..	.....	.....
Cd	Cd(NO <sub>3</sub> ) <sub>2</sub>	KCN in excess ..	5.0	.45	20°C.	Cd ..	.....	.....
Zn	ZnSO <sub>4</sub>	.....	2.5	.7	50°C.	Zn (dark) ..	.....	.....
Zn	ZnSO <sub>4</sub>	.....	3.5	1.2	25°C.	Zn (sponge) ..	.....	.....
Zn	ZnSO <sub>4</sub>	KCN in excess ..	5.5	.9	50°C.	Zn ..	.....	.....
Zn	Pb(NO <sub>3</sub> ) <sub>2</sub>	.....	3.5	.7	15°C.	Pb (dark) ..	PbO <sub>2</sub> ..	.....
Pb	Pb(CH <sub>3</sub> COO) <sub>2</sub>	Excess of CH <sub>3</sub> COONH <sub>4</sub> ..	3.0	.8	25°C.	Pb ..	.....	.....
Pb	Pb(NO <sub>3</sub> ) <sub>2</sub>	HNO <sub>3</sub> 10% ..	3.0	1.6	50°C.	.....	PbO <sub>2</sub> ..	.....
Mn	MnSO <sub>4</sub>	.....	5.0	1.3	15°C.	Mn (trace) ..	MnO <sub>2</sub> (trace) ..	.....
Mn	MnSO <sub>4</sub>	KCN 10% ..	3.5	.9	25°C.	Mn ..	MnO <sub>2</sub> ..	.....
Mn	MnSO <sub>4</sub>	{ CH <sub>3</sub> COONH <sub>4</sub> 5% Chromic alum 1% ..	3.5	.6	85°C.	.....	MnO <sub>2</sub> ..	Engels.
Ag	AgNO <sub>3</sub>	.....	3.5	.45	50°C.	Ag ..	AgO <sub>2</sub> (?) ..	.....
Ag	AgNO <sub>3</sub>	Excess of KCN ..	3.0	.25	15°C.	Ag ..	.....	.....
Sn	SnCl <sub>2</sub>	HCl 5% ..	2.5	.5	15°C.	Sn ..	.....	.....
Sn	SnCl <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> in excess ..	5.0	.4	15°C.	Sn ..	SnO <sub>2</sub> ppt. ..	.....
Sn	SnCl <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> and H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ..	3.5	.35	15°C.	Sn ..	.....	.....

\* The composition of these hydroxides has been determined by actual analysis by the method explained in Part II. of this paper.

The results obtained in these experiments are not very satisfactory as in nearly every case different conditions of current density obtained at different spots on the surfaces of the electrodes, and the phenomena observed were far from uniform. The classification of the results also is somewhat difficult as there is little apparent uniformity.

Taking the cathode reactions first one cannot fail to notice that when solutions of simple salts are electrolysed, very low current densities produce as a rule pure smooth deposits of the metal, but as the current density rises the deposits become spongy, and, particularly with Ni and Co, jelly-like deposits of the hydroxides are formed. It is particularly noticeable in the case of spongy deposits that the crystals which form the sponge appear to grow from isolated points and that the precipitation of the metal does not take place evenly on the whole surface of the electrode as though parts of the electrode became coated with some non-conducting substance. The causes producing this effect will be discussed more fully later in the paper.

With respect to anode reactions the chemical conditions under which precipitates are obtained vary considerably. With nickel and cobalt, for instance, anode precipitates are not produced under any conditions when simple salts are used, but are produced readily enough when sufficient ammonium sulphate or nitrate is added to produce the double salt, and disappear again on adding excess of the salt or of ammonia. With silver and lead on the other hand precipitates are produced on the electrolysis of the simple nitrates and with manganese on the electrolysis of any of its salts. It is further to be noted that all the metals which produce anode deposits are metals which have valencies of two or more orders of magnitude,

## PART II.

*It is proposed in this part of the paper to deal with each of the metals separately in order to simplify the tabulation of results which would be necessary if they were not dealt with separately.*

In order to be able to study the structure of some of the electrode deposits more closely than can be done in the cell previously described, an apparatus was devised whereby the electrodes could be examined under a low power objective. The results obtained by the use of this apparatus have been so remarkable that they occupy a large place in the work to be detailed.

The apparatus in its final form was constructed as follows:—

The electrolytic cell (Fig. 2a) consisted of a piece of vulcanite,  $\frac{1}{8}$  inch in thickness and  $1\frac{1}{2}$  by  $1\frac{1}{4}$  inches across. In the centre of this strip a hole  $\frac{1}{2}$  inch in diameter was drilled out and two small holes made, one on either side of the large one. Two fine holes were then drilled in the thickness of the vulcanite, each one passing from the outer edge of the strip through the small hole into the large one. Through these holes thin platinum wire electrodes were passed and allowed to project into the large centre hole. The diameter of the wire used was .093 millimetres and was chosen specially thin as it enabled the deposits on the electrodes, when transparent, to be more easily and thoroughly examined than when thicker wire was used. Bent copper wires were also pushed through the holes with the electrodes as far as the small holes in the vulcanite. The rest of the space in the holes carrying the electrodes were then filled with melted paraffin wax. This cell was then cemented with marine glue to a glass slide and placed on the stage of the microscope. To ensure a good connection between the platinum electrodes and the copper leads a drop of mercury was placed in each of the small holes. These two leads dipped into small cells made of paraffin wax and filled with mercury.



These cells were supported on a bracket fixed in front of the microscope stage. In this way a certain amount of play of the cell was allowed without interrupting the passage of the current during an experiment.

This cell was then connected up with a source of current (accumulator) capable of producing an E.M.F. of about 20 volts. In the circuit (Fig. 2b) there were placed a rheostat,  $R$ , giving resistances from 100-10,000 ohms, a reversing switch,  $W$ , and a galvanometer,  $G$ , which gave a readable

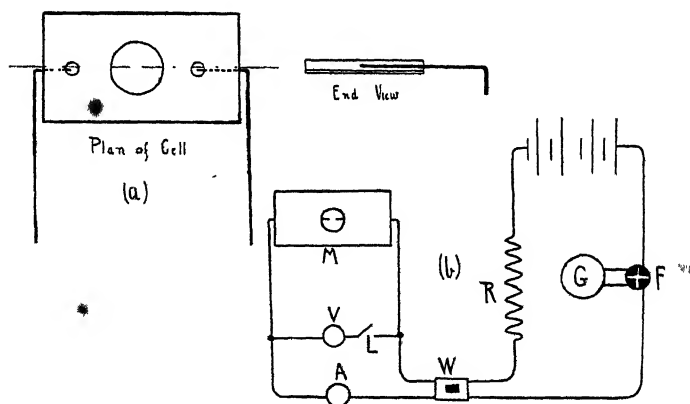


FIGURE 2.

deflection of 1-100 of a milliampere. The galvanometer was connected through a four-way switch,  $F$ , so that when necessary it could be cut out of the circuit. A delicate voltmeter was connected in a shunt circuit across the terminals of the cell and was provided with a cut-out switch,  $L$ , so as to remove it from the circuit when using the galvanometer.

Owing to the shape and size of the electrodes in this cell, the results obtained in it can in no way be compared with those obtained under the same conditions of current density and concentration of electrolyte when using a cell of ordinary dimensions, but the phenomena produced are in-

structive as showing the structure of the deposits and giving comparative values for the various salts used.

### CATHODE REACTIONS.

#### (a) *Cobalt Salts.*

When solutions of various salts of cobalt were electrolysed under the microscope, three different types of phenomena were observed, depending on the concentration of the electrolyte and the current density. These were:—

- (a) The formation of a compact metallic precipitate of cobalt on the cathode.
- (b) The formation of a dendritic metallic precipitate of cobalt on the cathode.
- (c) The formation of a blue gelatinous transparent film on the cathode.

The first or compact form was only produced when extremely minute currents (below .05 ampere per square decimetre) were passed through the solution. Under these conditions no observable quantities of gas were produced at the electrodes, but a gradual deposition on the cathode was made apparent by reading, at intervals of twelve hours, by means of an eyepiece micrometer, the diameter of the electrode, which, of course, slowly increased in thickness as the deposit was produced. The conditions under which the last two types of precipitate were formed will be seen from the tabulated results below. In order to note the effect, if any, of the anion with which the metal is combined the experiments were conducted with solutions of the sulphate, chloride and nitrate of cobalt. (These salts were all Kahlbaum's purest preparations.) The concentration of the solution is expressed in grams of the crystalline salt per 100 c.c.'s of the solution.

TABLE B.

Salt.	Concentration.	Volts.	Milli-amps.	Curr. Dens.	Result.
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	5 grs. per 100 cc.	8.9	1.52	1.013	Dendritic formation of metal and hydrogen.
"	"	6.2	.49	.327	Blue gelatinous film.
"	"	4.3	.30	.20	Torn off by gas.
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ...	5 grs. per 100 cc.	8.3	2.40	1.60	Dendritic metal and gas.
"	"	6.5	1.50	1.0	" "
"	"	3.8	1.30	.867	Dendritic metal first and then gelatinous compound.
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ...	5 grs. per 100 cc.	10.2	1.54	1.028	Dendritic metal and gas.
"	"	8.3	.84	.56	Blue gelatinous compound and gas.
"	"	6.5	.43	.286	" "
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.5 grs. per 100 cc.	13.0	1.45	.97	Dendritic metal first and then gelatinous compound.
"	"	10.3	1.15	.77	Blue gelatinous compound. Torn off by gas.
"	"	8.5	.65	.43	" "
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ...	2.5 grs. per 100 cc.	10.3	1.14	.76	Dendritic metal first and then gelatinous compound.
"	"	4.5	.16	.107	Blue gelatinous compound. Torn off by gas.
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.6 grs. per 100 cc.	16.0	1.80	1.2	Dendritic metal and then gelatinous compound.
"	"	10.3	.98	.65	Blue gelatinous compound.
"	"	8.5	.4	.266	" "
"	"	6.3	.16	.107	" "
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ...	.5 grs. per 100 cc.	8.5	.192	.128	Blue gelatinous compound and hydrogen.
"	"	4.5	.144	.096	" "

It is thus apparent that in the microscope cell the production of the dendritic metal depends on the current density only. When this rises above about .78 the metal is formed; below this, the blue hydrate is produced. The

effect of reducing the concentration of the solution is merely to lessen the conductivity and hence to reduce the current density at a given voltage. The nature of the anion does not affect the result, except that as their migration velocities are in the order  $\text{Cl}$ ,  $\text{NO}_3$ ,  $\text{SO}_4$ , greater concentrations are required with sulphates and nitrates to allow of the same current density at an equal voltage, than with the chloride.

A careful examination of the cathode wire, after these experiments, showed that compact cobalt metal was always deposited on it in small quantities at the same time as the production of the dendritic metal or the gelatinous precipitates took place. This was shewn to be the case by dissolving off the gelatinous compound or the dendritic metal with dilute hydrochloric acid. The current was then reversed through the cell for a few moments, and on testing the liquid with sulphuretted hydrogen the presence of cobalt was readily shewn.

The most striking phenomenon in the above experiments is the production of the gelatinous compound on the cathode. On first passing the current bubbles of gas come off rapidly and then a deep blue transparent solid makes its appearance. At the same time the galvanometer deflection steadily lessens till a definite minimum is reached, at which it remains practically constant. This compound appears to have, at a first glance, a crystalline structure, the outer edge being regularly dentated. Examination with a higher-powered objective shews, however, that this is due to the fact that the film is pierced with numerous fine holes, through which streams of hydrogen (see later) in minute bubbles make their way. The growth of the film being greatest between these holes, points are formed at fairly regular intervals, which give it the appearance noted (Fig. 6, a microphotograph of the film). This film, as previously noted, is deep blue in colour, but the moment the current ceases it turns green, beginning at the outer edges and spreading rapidly to the centre. When the current is turned

on again it instantaneously begins to turn blue from the electrode towards the outer edges. If a piece of the film is detached from the electrode it immediately turns green and remains green on standing any length of time. It dissolves in acids without the evolution of gas, and on standing in air shrinks and becomes opaque.

The compactness of the film varies very greatly with the concentration of the solution from which it is produced. When formed from a 10 per cent. solution of cobalt nitrate it is so compact that it is quite opaque, except at the extreme edges, and grows in nodular excrescences along the electrode; these excrescences forming around holes through which the gas can be seen escaping.

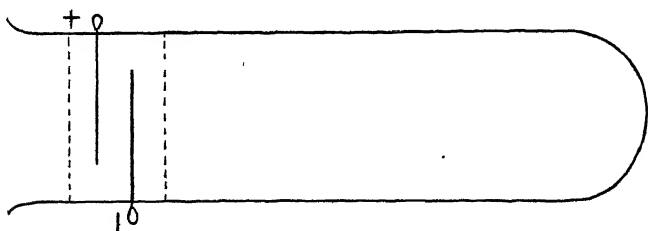


FIGURE 3.

As the concentration of the solution decreases, the film becomes more and more transparent and also considerably more porous and regular in outline.

The green compound was prepared in larger quantity and analysed in the following manner:—A boiling tube (Fig. 3) had two platinum wire electrodes fused in its sides in the manner shewn. This tube was then filled up to within half an inch of the electrodes with a 10 per cent. solution of cobalt chloride. Above this was floated sufficient of a 5 per cent. solution of the same salt to cover the electrodes to a depth of half an inch. A current at a pressure of 7.5 volts was then passed through the cell and the gelatinous compound which was formed on the cathode was torn off by the rush of gas and sank to the bottom of the denser solution. By renewing

the top layer of liquid from time to time about 1 gram of the precipitate was prepared and analysed. The object of the two layers of solution of different densities was to prevent, as far as possible, the acid liberated during the electrolysis from reaching the precipitate at the bottom of the tube.

The analysis of the precipitate was carried out by first washing it with cold water on a filter and then drying it in a vacuum dessicator over concentrated  $\text{H}_2\text{SO}_4$  for three days. A weighed quantity was then heated in a current of dry hydrogen to  $110^\circ \text{C}$ ., and the residue, after noting the loss in weight, analysed for cobalt. The residue proved to be cobaltous oxide and the composition of the precipitate, after the drying in the dessicator, is represented in the formula  $\text{Co}(\text{OH})_2, \text{H}_2\text{O}$ . The transparent precipitate produced on the electrode is probably much more highly hydrated than this, but no means could be found of proving it.

With a view of investigating the phenomenon of the change of colour in the film the following experiments were done:—

A good adherent film of the hydroxide was prepared by electrolysing a solution containing 3.5 grs. of cobalt nitrate per 100 c.c. of water. While the current was still passing the cell was irrigated with pure water till free from cobalt nitrate. During this process the film turned green and remained green, nor did it turn blue again, although the current was passed for some time. The cell was then washed with absolute-alcohol till free from water, and a dilute solution of anhydrous cobalt chloride in anhydrous acetone placed in it. When the current was passed through the solution, cobalt metal was deposited in patches round the film, but its colour remained unaltered. On removing some of the acetone and replacing it by water, the film again turned blue on passing the current. It is thus evident that both the ions of water and of the cobalt salt are necessary for the formation of the blue compound and that neither one without the other will cause it to form.

Before discussing the composition of this compound, it will be as well to recapitulate briefly some of the work done by previous workers on the colour of cobaltous salts. The greater part of this work deals with the production of blue substances either in solution, as when concentrated cobaltous chloride solutions are heated or mixed with alcohol, zinc chloride, calcium chloride, etc., or in the solid form, as when cobaltous chloride or sulphate is dehydrated.

Von Babo, in 1857, and Hartley (*Trans. Royal Dub. Soc.*, 1900), and many others have deduced proofs to shew that the colour of a cobaltous compound depends on the water of hydration (in Hartley's paper, from a study of the absorption spectra of solutions of the salts).

Engel (*Bull. Soc. Chim.*, 1891, 111, 6, 239) says that the change of colour on adding concentrated  $\text{HCl}$ ,  $\text{ZnCl}_2$ ,  $\text{CaCl}_2$ , etc., is due to the formation of double haloid salts, and he prepared double chlorides of cobalt and zinc and calcium.

Bersch (*Wien Akad. Sitzungsben.*, 867, 11, 56, 724) observed the formation of a blue lower hydrate from the hexahydrate at 30-35° C. and supposed that cobaltous salts could exist in isomeric modifications having different colours. Politizin shewed later, however, from a study of the solubility curves of the different varieties, that the colour changes were probably due to the formation of different hydrates, thus agreeing with Von Babo.

Ostwald (*Lehrbuch der Allgem. Chemie*) says that the blue colour is due to the non-ionised salt and the red colour to the ionised salt, and that mixtures of different proportions of these salts give rise to the scale of colours noticeable on gradually dehydrating the chloride. No practical data are offered, however, in support of the suggestion.

Donnan & Bassett (*J. C. S.*, 1902, *Trans.*, p. 939), from a study of the direction of migration flow of the coloured ions in an electrolytic cell, and other physical properties, arrive at the conclusion that the blue colour is due to anionic ions and the red colour to cationic ions of cobalt. In the case of

chloride of cobalt, for instance, the red solutions contain cobalt chloride in the form  $\text{Co}^{++}\text{Cl}_2^-$ , whereas the blue solutions may contain such complexes as  $\text{Co}^{++}\text{CoCl}_4^-$ . The formation of complex ions in solution undoubtedly plays a very important part in inorganic chemistry, and the later researches of Steele and Biltz make it almost certain that the conclusions of Donnan & Bassett are correct.

Although the unstable blue compound formed at the cathode during these experiments is nothing like the blue cobaltous salts described above in chemical properties, yet the close resemblance in colour makes it probable that similar theories would explain it.

As the hydrate is insoluble in water, the theory of Ostwald as to differences in ionisation may be dismissed. It is difficult also to see how the theory of hydration of the molecules can hold good in this case, as, although there is a stream of water molecules passing through the pores of the film (due partly to endosmose and partly to convection), it has been shewn experimentally that when the cell contains water only, and even water containing a trace of HCl, the green hydrate remains unaltered when the current is passed. It seems much more likely that the green hydrate in the presence of continuously uniting ions of cobalt and hydroxyl becomes converted into a complex cobaltous hydrate of such a formula as  $\text{Co}^{++}\text{Co}(\text{OH})_4^-$  or  $\text{Co}^{++}(\text{Co}^-[\text{OH}]_3)_2$ , and that on the cessation of the current this unstable substance resolves itself into the ordinary green forms  $\text{Co}^{++}(\text{OH})_2$ .

It has been shewn (Marshall, J. C. S., *Trans.*, p. 760, 1891) that cobaltic salts, on the other hand, are blue in colour and extremely unstable, and in view of the fact that by the electrolysis of ferric chloride solutions (see this) ferric hydroxide is obtained on the cathode, it might be supposed that the blue hydroxide was a cobaltic compound. Ferrous salts, however, have been shewn to give the green ferrous hydrate until some of the salt is oxidised at the anode and



diffuses to the cathode, and it is not possible that a cobaltous salt could produce a cobaltic compound at the cathode immediately on passing the current.

*Experiments with the Large Cell* (page 188).—In the experiments conducted with this cell it was found possible to produce exactly the same phenomena as with the small cell, although the conditions varied considerably. With solutions of cobaltous salts ranging in strength from 3 to 5 per cent., as long as the current density was kept below .8, at laboratory temperatures a compact but somewhat dark deposit of the metal was obtained. Above this, however, the hydrate invariably made its appearance in patches of a somewhat indistinct colour, probably a mixture of the blue and green compounds, and at the edges of the electrode, where the current density was greatest the metal in dendritic form made its appearance.

*Anode.*—When electrolysing solutions of cobalt ammonium sulphate or nitrate a black powdery and non-adherent precipitate, which was not analysed but is stated by Classen to be  $\text{Co}_2\text{O}_3$ , made its appearance at the edges of the anode when the current density was above 1.2.

(No comment is made here on the reactions taking place at the electrodes; this is better left till all the experimental work has been detailed.)

*Effect of Hydrochloric Acid and other Acids on the Formation of the Hydroxide at the Cathode.*—In order to test the effect produced by adding acids to the solutions of salts under examination a number of experiments were done with solutions of different concentrations containing known quantities of the free acid. One effect is, of course, to increase the conductivity of the solution very greatly, but in addition to this, it has the effect of preventing the formation of the hydroxide when the percentage of the acid reaches about 2, and with quantities equivalent to 4 per cent., and over, the formation of the dendritic metal is also prevented, only the compact metal being deposited so far

as can be seen. In experiments conducted on a larger scale the solvent action of the acid must be taken into consideration as during the deposition of the metal, a stage of concentration will eventually be reached when the metal is dissolved from the electrode as fast as it is deposited. The following are the results obtained in one experiment with the microscope cell using solutions of  $\text{CoCl}_2$ , containing free  $\text{HCl}$ .

TABLE C.

Conc. of Solution.	Per cent. of $\text{HCl}$ .	Volts	Milliamps.	Result.
8 grs. per 100 cc.	5	6.0	Too high for galvanometer	Steady stream of gas. Gradual thickening of electrode.
„	2	4.3	71 milliamps	Dendritic metal forms and a good deal of gas.
5 grs. per 100 cc.	1	8.3	2.5 „	Dendritic metal at front and hydrate at end of electrode.
„	1	6.0	.65 „	Dendritic metal and a trace of hydrate.
„	1	4.3	.32 „	Metal and hydroxide were deposited side by side, forming a bushy dendritic deposit round the electrode, with the jelly-like hydroxide between the crystals of the metal.

(b) *Nickel.*

Experiments done with the microscope cell.

The salts used in these experiments were  $\text{NiSO}_4$ ,  $7 \text{H}_2\text{O}$ ,  $\text{NiCl}_2$ ,  $6 \text{H}_2\text{O}$ , and  $\text{Ni}(\text{NO}_3)_2$ ,  $6 \text{H}_2\text{O}$ . Unlike cobalt, only two types of deposit were obtained on the cathode, (a) a compact deposit of metallic nickel, and (b) a green gelatinous compound, which does not alter in colour on cutting off the current or on allowing it to stand. This green compound was obtained and analysed in the same way as the corresponding cobalt compound and when dried in a vacuum dessicator over concentrated  $\text{H}_2\text{SO}_4$  proved to have the com-

position  $\text{Ni}(\text{OH})_2\text{H}_2\text{O}$ . In the following table of results only those obtained by the electrolysis of nickel sulphate are given, the others agreeing in the same manner as with cobalt.

TABLE D.

Salt.	Concentration.	Volts.	Milli-amps.	Curr. Density.	Result.
$\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ ...	10 grs. per 100 cc.	17.5	2.50	1.66	Green hydroxide formed & hydrogen.
" ...	"	15.0	1.88	1.25	" "
" ...	"	13.0	1.72	1.15	Green hydroxide formed. Blown off electrode by gas.
" ...	"	8.5	.90	.60	" "
" ...	"	6.3	.82	.55	" "
" ...	"	4.0	.16	.105	" "
$\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ ...	5 grs. per 100 cc.	8.3	.71	.47	" "
" ...	"	6.3	.41	.29	" "
" ...	"	3.9	.192	.13	" "
" ...	2.5 grs. per 100 cc.	8.5	.49	.326	" "
" ...	"	6.3	.25	.166	" "
" ...	"	3.9	.09	.060	" "
" ..	1.0 grs. per 100 cc.	8.5	.24	.160	Green hydroxide formed. Sticks to electrode.
" ...	"	6.3	.16	.106	" "
" ...	"	3.9	.07	.011	" "

Although numerous experiments were done, the dendritic metallic deposit was not obtained either with the nitrate or the chloride of the metal.

*Experiments with the Large Cell.*—Reference to Table "A" (page 189) will show that solutions of pure nickel sul-

phate could be made to give good clear deposits of nickel as long as the current density was kept below 1.0. When it rose above this the effect was the same as with the metal cobalt, the green gelatinous precipitate or nickelous hydrate being produced in patches and a deposit of the dendritic metal formed along the edges of the electrode. The electrode exhibited also a deposit of compact nickel on its surface when the upper layer of hydroxide was removed with weak acid. The dendritic metal, however, was neither so easily nor so frequently produced as in the case of the cobalt salts.

*Anode Reactions.*—The electrolysis of a solution of nickel ammonium sulphate in this cell produced, at current densities above 1.2, a black powdery deposit on the anode, particularly at the edges of the electrode. Several experimenters (Classen, Moore, and others) have analysed this deposit and found it to consist of a mixture of  $\text{Ni}_2\text{O}_3$  and  $\text{NiO}_2$ . An excess of ammonium sulphate, however, entirely prevents this deposition from taking place. Using nickel ammonium nitrate instead of the sulphate it was found possible to produce the same deposit at current densities as low as .95. It was noticed that, during the experiments done with nickel ammonium sulphate containing an excess of ammonia, the current density, which was kept at about 1.3, showed a regular increase and decrease of about .3 amperes as though the resistance of the cell was constantly and regularly altering. A search through the literature of the subject brought to light the fact that Thiel and Windelschmidt (*Zeitsch. Electrochem.*, 1907, 13, 317) found that periodic differences in the current strength and potential at the anode were produced during the electrolysis of solutions of nickel ammonium sulphate. This they explained as being due to the alternate production of non-conducting  $\text{Ni}(\text{OH})_2$  on the anode and its subsequent solution in the ammonia. They found no alteration in the potential at the cathode. They assumed that the nickel in solution is

chiefly present in the form of a complex ion  $\text{Ni}(\text{NH}_3)_x^{2+}$  and a little  $\text{Ni}^{2+}$ . This latter is oxidised at the anode to the hydroxide  $\text{Ni}(\text{OH})_2$  and is deposited. This hydroxide is dissolved by the ammonia and the nickel converted into the complex ion  $\text{Ni}(\text{NH}_3)_2^{2+}$ . They find the periods most sharply defined when the current density is about 1.0. This phenomenon of what may be called catalytic anodic pulsations is of very great importance as it shows regular changes in the composition of the layers surrounding the anode. It is doubtful as to whether or not Thiel and Windelschmidt's explanation is the correct one as it does not fit in readily with the known facts concerning anodic oxidation. Elbs (*Zeit. Electrochem.*, 1905, 11, 809) produced a deposit on the anode of regular composition by the electrolysis of nickelous sulphate kept constantly neutral by the addition of caustic soda. This was analysed after drying in a vacuum dessicator and found to have the composition  $\text{Ni}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  when the pressure in the dessicator was from 7.3 mm. and  $\text{Ni}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  when less than 3 mm.

During some of the experiments with the microscope cell, it was noted that if a green film of the hydroxide was slowly produced from nickel sulphate solution and the current then reversed, the film became rapidly opaque and brown in colour, the change taking place from the wire towards the outside in a few seconds. This result could not be repeated on a larger scale although several attempts were made, and hence the substance could not be analysed. It is probable, however, that the change is one of oxidation and that the new substance is nickelic oxide, the change taking place being somewhat like that produced during the charging of an Edison accumulator.

#### (c) Iron.

The salts used were ferrous sulphate, ferric chloride and ferric sulphate.

*Experiments with the Microscope Cell.*—As with cobalt the cathode deposits were obtained in three forms, the

compact metallic form, the gelatinous hydroxide and the dendritic metal.

TABLE E.

Salt Used.	Concentration.	Volts.	Milli-amps.	Curr. Density.	Result
$\text{FeSO}_4\cdot 7\text{H}_2\text{O}$	... 5 grs. per 100 cc.	8.6	1.05	.70	Dendritic metal.
"	...	6.3	.57	.38	" "
"	...	4.0	.144	.096	" "
"	... 2.5 "	8.5	.256	.170	Metal produced first and then green hydrate.
"	...	6.4	.176	.116	" "
"	...	4.0	.096	.064	Metal and "hydrate produced simultaneously.
"	... 1.5 "	8.5	.288	.192	A trace of metal and mostly hydrate formed.
"	...	4.0	.080	.033	Pale green hydrate and gas only.
$\text{FeCl}_3\cdot 6\text{H}_2\text{O}$	... 1.0 "	8.5	.452	.30	Metal in dendritic form.
"	...	6.5	.340	.277	" "
"	...	4.0	.30	.200	" "
$\text{FeCl}_3\cdot 6\text{H}_2\text{O}$	... .5 "	8.5	.4	.270	Metal only.
"	...	6.5	.23	.153	Metal and a little red ferric hydrate formed.
"	... .25 "	8.5	.128	.085	A little metal, mostly the red hydroxide.
		4	.032	.021	Practically all red hydroxide and hydrogen.
$\text{Fe}_2(\text{SO}_4)_3$	... .25 "	8.5	.160	.107	Metal and red hydrate together.
Anhydrous	... .125 "	8.5	.09	.060	Red hydroxide only and hydrogen.
"	...	6.5	.048	.032	" "
"	...	4	.032	.021	" "

From the above results it is seen that the conditions of current density are very much lower than is the case with nickel or cobalt, so that the hydroxide may be produced. Apparently, also, ferric salts give the compound only at very much less concentrations than the ferrous salts. This is due, however, to the difference in the conductivities of the

solutions as in all cases with a current of .3 milliamperes and above the dendritic metal was formed; between .3 and .12 milliamperes the metal and hydroxide were both formed, and below .12 the hydroxide only.

Owing to the low conditions of current density necessary it was found impossible to produce the hydroxides on a larger electrode (either wire or disc) without producing some of the metal with it at the same time. It has, therefore, proved impossible to analyse the compounds in question. That they are hydrated hydroxides, however, may be reasonably supposed in view of the following facts:—

- (a) They are produced by the same methods as the corresponding compounds of cobalt and nickel, which have been analysed.
- (b) They are dissolved by acids without the evolution of gas, and become opaque on standing in air.
- (c) They have the same colours as the known hydroxides, viz., green from a ferrous compound, and red from a ferric compound.

A rather unexpected fact is the production of the red ferric hydrate at the cathode when electrolysing solutions of ferric salts. Its production, however, affords convincing proof of the fact that although the formation of these hydroxides takes place in the neighbourhood of the cathode they are not formed actually on the cathode itself, else, in this case, the iron ions would first suffer reduction to the ferrous condition and ferrous hydroxide would result.

It was further noticed that during the electrolysis of solutions, of such concentration of both ferrous and ferric salts, that both metal and hydroxide were formed, that the metal gradually became converted into the hydroxide on standing, the ferric hydroxide being formed, however, in both cases. This is probably due to the action of the faintly acidified water in the cell, and the ferric compound is formed in both cases because of the dissolved oxygen in the solution of electrolyte.

*Experiments with the Large Cell.*—If the results of the five experiments, quoted in Table "A," be examined it will be seen that as was the case with the previous metals no anode deposit is formed when the simple metal salts are used, but these deposits are produced when a double is used. The presence of an oxidising agent, such as nitric acid, helps the reaction and a high current density (above 1·3) is also necessary to produce the deposit. If an excess of the salt forming the double compound is used the formation of the deposit is prevented. The ferric hydroxide formed is non-adherent and floats about in the liquid.

(d) *Zinc.*

In these experiments zinc sulphate and zinc chloride were used.

*Experiments with the Microscope Cell.*—

TABLE F.

Salt.	Concentration.	Volts.	Milli-amps.	Current Density.	Result.
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	2·5 grs. per 100 cc.	8·5	1·30	·87	Dendritic metal, unaltered on standing.
"	"	6·3	·95	·633	" "
"	"	3·9	·25	·166	" "
"	·5 "	8·5	·122	·746	Dendritic zinc formed. On standing this slowly turned to hydrate.
		3·9	·032	·021	Dendritic metal and some hydrate. Metal disappears as hydroxide on standing.
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	·25 "	8·5	·85	·566	Trace of Zinc. Mostly hydroxide.
		3·9	·021	·015	Hydroxide only formed.

The outstanding fact in the above experiment is the change which the metallic zinc undergoes on standing. If a solution of zinc sulphate containing about ·7 grammes per



100 c.c., for instance, be electrolysed at different current densities, the dendritic metal produced has a different appearance. With high densities the metal deposits in long single filaments (Figs. 4*a* and 7), and in this form it readily attacks water and is converted into a colourless transparent solid, supposedly the hydrate. When, however, lower densities are used the metal forms true dendritic crystals

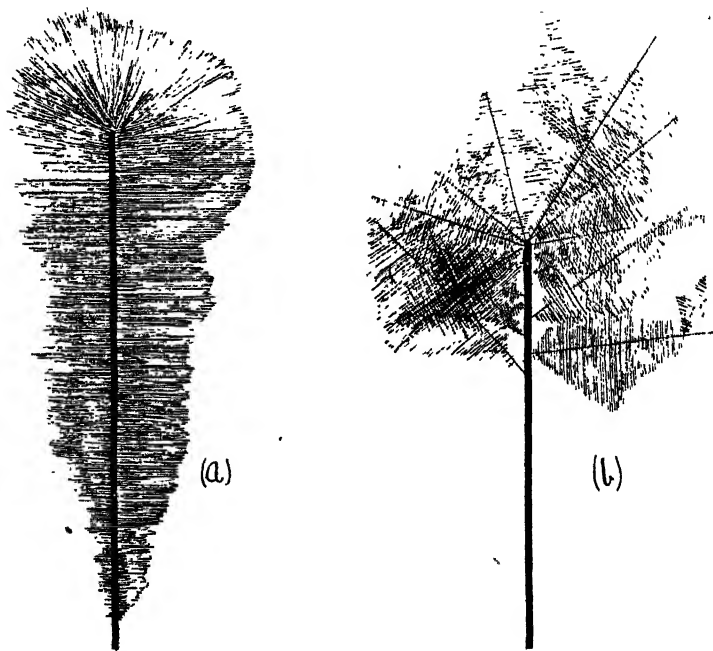


FIGURE 4.

having a "telegraph pole" structure (Figs. 4*b* and 8) and these crystals, which are much more solid in appearance, do not change at atmospheric temperatures. If, however, the temperature of the contents of the cell be raised somewhat by means of a piece of hot glass rod these crystals also become transformed into the gelatinous hydroxide. Knowing that hydrogen peroxide was one of the products of the interaction

of zinc dust and water, the cell contents were tested for this substance but without success.

*Experiments with the Large Cell.*—When solutions of zinc sulphate are electrolysed there is always a deposit of zinc produced on the cathode. The character of the deposit, however, varies very much with the current density and the composition of the electrolyte. With current densities above 1.0 the zinc is spongy and non-adherent. Quantitative experiments have shown that this sponge is always heavier than the theoretical amount and various experimenters (Kiliani and Mylius and Fromm, see below) have established the presence of zinc oxide in the dried deposit. In view of the phenomena observable in the microscope cell the presence of this zinc oxide is explained by the production of zinc hydrate from the solution, when, towards the end of the deposition, it becomes sufficiently dilute, or at moderately high temperatures, by the action of the dendritic metal composing the sponge, on the water. (A cylindrical platinum electrode covered with spongy zinc and immersed in distilled water gave at the end of 12 hours distinct indications of the formation of  $H_2O_2$ ).

The conditions governing the production of spongy zinc have been fully worked out by the following experimenters:—

Kiliani—*Berg und. Huttemm Ztg.*, 1883, p. 250.

Nahnsen—*Berg und. Huttemm Ztg.*, 1891, p. 393.

Mylius and Fromm—*Zeit. fur Anorg. Chem.*, 1895.

Their results shew that high temperatures, oxidising agents, and the presence of metals more electronegative than zinc and very dilute solutions, cause the formation of sponge.

Nahnsen gives in tabular form the results of electro-deposition of a 5 per cent. solution of the double cyanide which gives a graphic idea of the effect of temperature and current density on the deposit.

Current Density per Square Metre.	0° C.	10° C.	25° C.	36° C.
10	F.	I.S.	S.	S.
50	F.	I.S.	I.S.	S.
100	F.	F.	S.	I.S.
150	F.	F.	F.	S.
200	F.	F.	F.	F.

F. = Firm deposit. S. = Sponge. I.S. = Incipient sponge.

*Anode Reactions.*—Under no conditions are anode deposits formed.

(e) *Cadmium.*

*Experiments with Microscope Cell.*—The substances used were cadmium sulphate and cadmium nitrate. Only those results obtained with cadmium nitrate are given in the following table.

TABLE G.

Salt.	Concentration.	Volts.	Milli-amps.	Current Density.	Result.
$\text{Cd}(\text{NO}_3)_2$ ...	·5 grs. per 100 ccs.	8·4	1·35	·90	Dendritic metal, not altered on standing.
„	„	6·2	·56	·375	„ „
„	„	3·9	·26	·175	„ „
$\text{Cd}(\text{NO}_3)_2$ ...	2·5 „	8·3	·96	·640	„ „
„	„	6·3	·63	·420	„ „
„	„	3·9	·23	·153	„ „
„	·5 „	8·5	·61	·407	Dendritic metal formed. Turned rapidly to hydroxide on standing.
„	„	3·9	·065	·043	Do. do. but the crystals of metal were coarser and did not change so rapidly to hydroxide.
„	·1 „	8·5	·025	·016	Dendritic metal and hydroxide. Metal rapidly alters.
„	„	3·9	·010	·0066	Hydroxide only formed.

The reactions of cadmium salts are very like those of zinc. The dendritic metal tends to form the hydroxide, but rather more readily than zinc (Figs. 9 and 10). The condition of current density and hence of concentration at which the hydroxide is primarily produced are different to those for zinc. It was only when solutions containing .1 grs. per 100 c.c. were electrolysed that it was found and then only with a current density of .016.

*Anode Reactions.*—As with zinc anode deposits are not produced under any conditions.

*Experiments with Large Cell.*—The reactions taking place are so similar to those of zinc that no comment is required.

#### (f) *Lead.*

*Experiments with the Microscope Cell.*—Solutions of lead nitrate of concentrations varying from 5 to .05 grs. per 100 c.c. were electrolysed. Dendritic lead crystals were obtained under all conditions. Owing to the importance of being able to recognise very dilute solutions of lead salts, experiments were done with solutions in which the concentration varied from 10 to 1 part of lead per million. With the solutions containing 10 to 7 parts of the metal per million, distinct dendritic deposits were obtained but below this concentration one of two things happened. A minute whitish deposit (lead hydroxide?) formed on the cathode, or else a brown deposit, easily distinguishable, appeared in the liquid round the cathode. What this is, it is impossible to say.

When solutions containing more than three grams of lead per 100 c.c. were electrolysed at current densities above 1.0, a brown deposit (presumably lead peroxide) appeared at the anode.

*Experiments with the Large Cell.*—The outstanding feature in these experiments is the fact that simple lead salts, particularly the nitrate, form anode deposits. The formation of this deposit is considerably helped by the presence of oxidising agents such as nitric acid. There is a tendency

for the lead produced at the cathode at high current densities to form a sponge. This sponge suffers from the disadvantage of being non-adherent to the electrode but is quite pure in composition.

Elbs and Ritson (*Zeit. Electrochem*, 1903, 9, 267-268) have shown that spongy crystals of lead are always due to the presence of plumbic ( $\text{Pb}^4$ ) salts in solution. When these are destroyed firm deposits are produced.

The formation of lead peroxide at the anode during the electrolysis of lead salts has been very fully dealt with in the work done on the theory of lead accumulators. The following views expressed on the formation of the peroxide are of value.

C. Liebenoff (*Zeit. Electrochem*, 1896, 2, 420) considers that action of the charging current is to produce ions  $\text{Pb}\bar{\text{O}}_2$  and  $\text{Pb}^{++}$  in solution. The  $\text{Pb}\bar{\text{O}}_2$  ions on discharge at the anode become lead peroxide.

Loeb (*Zeit. Electrochem*, 1896, 2-495) agrees with Liebenoff, but regards the primary decomposition of water as essential to the formation of the  $\text{Pb}\bar{\text{O}}_2$  ion.

Elbs (*Zeit. Electrochem*, 1896, 3, 70) quotes Le Blanc, who regarded the passage of the current as producing a change in the valency of the lead from  $\text{Pb}^2$  to  $\text{Pb}^4$  at the anode. From observations of the reactions taking place at the anode during the electrolysis of acetates of various metals he classified them as follows:—

ANODE REACTION.	CLASS OF METALLIC ACETATE.
Group I.—Ethane and $\text{CO}_2$ formed ... ..	Acetates of metals of constant valency.
Group II.—Mainly oxygen formed ... ..	Acetates of metals which are bi and trivalent and which yield less stable higher than lower salts.
Group III.—No gas produced ... ..	Acetates of metals of valencies between 2 and 4, which form comparatively stable peroxides.

From this he concludes that during the electrolysis of lead acetate, lead peroxide is formed due to the production of the tetracetate which breaks down to the peroxide and acetate as fast as formed.

Liebenoff (*Zeit. Electrochem.*, 1896, 2, 653) describes the following experiment:—The vessel (Fig. 5*a*) contains N

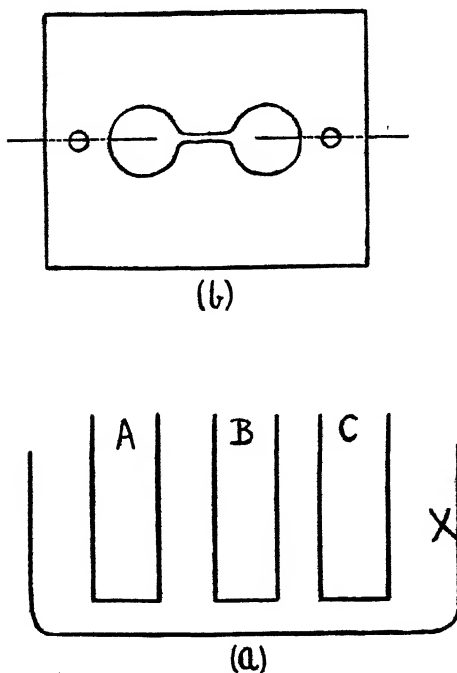


FIGURE 5.

alkali saturated with  $\text{PbO}$ . A, B, and C are cylinders, closed at the bottom by a membrane and containing N alkali *only*. Vessel A contains a platinum cathode and vessel C a platinum anode, vessel B serving to measure the rate of diffusion. A large quantity of lead was found in the anode vessel and none in the cathode vessel. He supposes that this is due to  $\text{Pb}(\text{OK})_2$  giving  $\text{Pb}\bar{\text{O}}_2$  and  $2\text{K}^+$ .

(This experiment has been done by several experimenters with the same result, but a solution admittedly containing potassium plumbate  $\overset{++}{K}_2 \overset{--}{Pb} \overset{--}{O}_2$  cannot be compared with, say,  $\overset{++}{Pb} (\overset{-}{NO}_3)_2$  in which the lead is in the cation).

Foerster (*Zeit. Electrochem*, 1897, 3, 525) discusses Le Blanc's and Liebenoff's and Loeb's views. Agrees with Le Blanc and cites the formation of ammonium lead chloride  $(\overset{+}{NH}_4)_2 \overset{+}{Pb} \overset{+}{Cl}_2$  by the electrolysis of  $\overset{+}{NH}_4 \overset{-}{Cl}$  and  $\overset{+}{Pb} \overset{-}{Cl}_2$  at  $0^\circ \text{C}$ .

#### (g) Manganese.

*Experiments with Small Cell.*—Owing to the action taking place at the anode wire the reaction at the cathode was obscured in the ordinary cell and could not be followed. A double cell of the form shewn in Fig. 5b was therefore constructed. With this it was noted that with concentrations above 2 per cent. of manganese sulphate and at all current densities no deposit was obtained. Below this concentration, however, brownish gelatinous hydroxide(?) made its appearance but only in very small quantities. At the anode, however, under all conditions of concentration and current density a thick pale brown precipitate made its appearance. When dilute solutions (25 per cent. of  $\overset{+}{Mn} \overset{-}{SO}_4$ ) were used a purple fluid could be observed streaming from the anode and rapidly disappearing, giving place to the brown peroxide. The colour of this substance shews it to be probably the unstable permanganic acid. Little or no work seems to have been done to confirm this. Georg von Knorre (*Zeit. Electrochem*, 1897, 3, 312) refers to the formation of permanganic acid when  $\overset{+}{Mn} \overset{-}{SO}_4$  is added to an accumulator. Other experimenters take its composition for granted.

#### (h) Tin.

$\overset{+}{Sn} \overset{-}{Cl}_2$  dissolved in the most dilute solution of hydrochloric acid possible was used.

*Experiments with Small Cell.*—At all concentrations and current densities only crystalline tin was formed.

*Experiments with Large Cell.*—HCl solutions of  $\text{SnCl}_2$  give clean deposits of metallic tin under all circumstances. These deposits are always, however, highly crystalline. When stannous chloride was dissolved in ammonium oxalate, and the solution electrolysed with a high current density,  $\text{SnO}_2$  was formed at the anode, and, being non-adherent, floated in the solution.

#### CATHODE REACTIONS OF THE METALS Co, Ni, Fe, Zn, Cd, Mn, Pb, AND Sn.

The experiments with the microscope cell have shewn that it is possible to obtain from a number of these metals (Co, Ni, Fe, Zn, Cd, Mn and doubtfully Pb) either the pure metal or the hydroxide deposited on the cathode. The conditions of concentration and current density affecting the production of these substances have also been noted, and it has been found that as we proceed along the list of metals in the order written that the dilution necessary to produce the hydrate increases and the limit of current strength decreases.

Before considering the conditions of hydroxide production in detail, the formation and structure of these substances, as revealed by the microscope, should be noted. In the first place, the hydroxide of the metal is not produced as a secondary reaction of the deposited metal of the cathode, but is a precipitate from the electrolyte in the cathode area. This is shown by the following considerations.

(a) In those experiments in which the hydroxide was produced a fall in current density always accompanied the accumulation of the film. This shows that the hydroxide is non-conducting and acts by increasing the resistance of the electrolytic cell, being in fact a semipermeable membrane. The platinum wire must, therefore, remain the electrode and not the film. The hydroxide as it forms, however, continues to be produced on the outside of the film



(this can be seen to take place) and not on the electrode, as would be the case if the metal were deposited primarily first.

(b) During the electrolysis of iron salts it was shown that ferrous salts produced ferrous hydroxide, and ferric salts ferric hydroxide at the cathode, thus proving in the case of ferric salts at least that the ferric hydroxide had been produced from the  $\text{Fe}^{+++}$  ions before they reached the cathode, as on reaching the electrode they would become  $\text{Fe}^{++}$  ions.

To produce hydroxides a concentration of hydroxyl ions must exist in the neighbourhood of the cathode, so that the metal ions meeting them may give up their ionic changes and combine with them. The production of hydroxyl ions in any quantity must necessitate the liberation of hydrogen at the cathode in order to release them, as the ionisation of water is itself small. The conditions under which hydrogen is liberated at the cathode will therefore determine in part the production of the hydroxide.

The potential difference,  $e$ , between cathode and electrolyte during the deposition of a metal is given by the equation—

$$e = \frac{RT}{nF} \log_e \frac{P_m}{pm}$$

where  $R$  is the gas constant,  $T$  absolute temperature,  $n$  the valency of the metal,  $F$  the electrochemical constant, and  $P_m$  the electrolytic solution pressure of the metal, and  $pm$  the osmotic pressure of the ions. As  $p$  becomes less during the deposition of the ions or the dilution of the solution the potential difference rises in consequence, so that the difference of potential between the cathode and the electrolyte necessary to precipitate the metal increases with increasing dilution. In the case of the metals studied this potential difference is always greater than that theoretically required for hydrogen to be liberated, as they occur above hydrogen in the tension series, but owing to the low concentration of

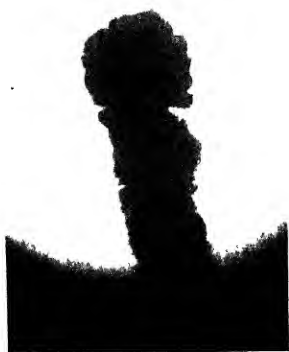


FIG. 6.



FIG. 7.



FIG. 8.



FIG. 9.



FIG. 10.



hydrogen ions it is possible, by keeping the current density, and hence the cathode potential, as low as possible, to liberate the metal without much hydrogen. This can even be shown in the microscope cell. With very dilute solutions in which the concentration of the metal ions approaches that of the hydrogen, the tendency will be in all cases to produce the hydroxide, as hydroxyl ions will be liberated at a rate approaching that of the metal.

It has been shown, however, that there is a greatly varying range of current density over which the hydroxide of the metals may be produced. This appears to be due to what is termed the over pressure or over voltage for the metal in question and refers to the excess voltage (between the electrode and electrolyte) necessary to liberate hydrogen on a surface of that metal over that necessary to liberate it on a reversible electrode. (Le Blanc, *Electrochemistry*, p. 287.) This differs in different metals. It has not been possible to compile an exact table of these excess potentials, as very different values are assigned to them, but they occur roughly in the order Ni, Co, Fe, Zn, Cd, Pb and Sn, that of nickel being least and tin greatest. If the over-voltage for a metal be represented by  $n$  then the potential required to liberate hydrogen at a cathode covered with that metal will be represented by the equation—

$$e = \frac{RT}{F} \log_e \frac{P_{H_2}}{P_H} + n$$

If it be supposed, therefore, that a fairly concentrated solution of a salt be taken and a current of constantly increasing density be passed through it, a point will be reached at which the potential between the cathode and electrolyte will just be sufficient to liberate the metal. This potential is, as explained before, given by the formula—

$$\frac{RT}{nF} \log_e \frac{P_m}{pm}$$

If, however, the solution is now diluted, either by adding water or continuing the electrolysis, owing to the decrease of

the osmotic pressure of the metal ions, the potential will gradually rise till a point is reached at which the cathode potential is sufficient to liberate hydrogen, then—

$$e = \frac{RT}{nF} \log_e \frac{P_m}{pm} = \frac{RT}{F} \log_e \frac{P_{H_2}}{pH} + n$$

A concentration of OH radicles will now take place in the cathode area and the hydroxide of the metal will be formed. If  $n$  is small, as with nickel, the evolution of hydrogen will begin with the deposition of the metal, but if it be large, provided the solution is not too dilute, the metal may be deposited without hydrogen, and therefore without the formation of hydroxide.

A reference to the table of results previously enumerated will show, however, that given a solution of such a concentration that the hydroxide can be produced from it, it is generally possible, by increasing the current density, to reach a point at which the hydroxide apparently ceases to be produced and the metal only is formed. For instance, with cobalt salts (Table "C") the dendritic metal is always produced when the current density rises above 1.2, whatever the concentration may be. This marks the point at which, owing to the scarcity of the hydrogen ions, the greater part of the current is being carried by the metal ions and some of the metal becomes deposited with the hydroxide. As the current increases the proportion of metal deposited will gradually become greater, but a proportion will still be the hydroxide. A careful examination of the deposits formed under these conditions has shewn, in fact, that when a dendritic deposit is formed at a concentration at which the hydroxide can be produced by decreasing the current density, this deposit always contains a little of the gelatinous hydroxide, thus the deposits of dendritic cobalt referred to above always contained some of the hydroxide, and as the concentration and consequently the current density decreased the hydroxide alone was finally produced.

The simultaneous production of the metal and hydroxide on a larger electrode, a phenomenon which continually occurs during the electrolyses of simple salts of the metals when the current density gets too high, may, in view of the above facts, be readily explained. Those parts of the electrode which become coated with the hydroxide (it is probably formed all over it at first and then blown off in places by the escape of hydrogen) are practically insulated and a rise in current strength takes place in the exposed parts, with the result that a mixture of the dendritic metal and the hydroxide is precipitated at these points. It is a generally accepted fact that spongy or dendritic metallic deposits contain small quantities of hydrides of the metals. This is pure hypothesis, and the difficulty of producing these compounds, and their instability when produced, makes the chances for their formation very remote.

It is much more likely, in view of the fact that the hydroxides of nearly all the metals above hydrogen in the tension series can be formed at the cathode, that the spongy metallic deposits produced by the use of too high current densities, contain the hydroxides of the metals as impurities, if they contain any impurities at all.

It is not within the scope of this paper to deal with the chemical reactions taking place at the cathode when complex metallic salts are used for electrolysis, but the effect of using an acid solution of the salt might be briefly noted.

When an acid is added to the electrolyte the conductivity of the solution and the concentration of the hydrogen ions becomes greatly increased. Hydrogen therefore will be produced more readily at the cathode, but as the hydrogen ions are supplied by the acid the concentration of hydroxyl ions in the cathode area will remain stationary. The tendency to form the hydroxide therefore decreases as the amount of acid increases. Added to this there is, of course, the actual solvent action of the acid on the hydroxide to be considered, so that with about 3-4 per cent. of acid in the

solution, if any hydroxide were formed, it would be dissolved at once.

It must be evident that much more information could have been obtained as to the limits of hydroxide formation in the above paper if the actual potentials at the cathode had been given. Up to the present, however, the results obtained in these determinations have been extremely unsatisfactory, as the formation of the hydroxide in patches on the surface of the electrode, and the alterations in current density which take place, make the readings obtained of no value. Further work is, however, being done in this line.

## NOTE ON THE PREPARATION OF BENZYL MERCAPTAN.

By J. A. SMYTHE, Ph.D., D.Sc.

[Read May 16th, 1912.]

The necessity for preparing considerable amounts of benzyl mercaptan has led the author of this note to try various methods, some results of which are put on record in the hope that they may be of use to others working in this field.

The ordinary method of preparation consists in the action of benzyl chloride on an alcoholic solution of sodium sulphhydrate. This is best carried out as follows:—100 grams of the commercial crystallised sodium sulphide,  $\text{Na}_2\text{S}$ , 9  $\text{H}_2\text{O}$ , are dissolved by gentle heating in 800 c.c. of alcohol to which 50 c.c. of water are added. The solution is saturated quickly (within six hours if possible) with hydrogen sulphide, then 80 grams of benzyl chloride are added in portions, the mixture being well shaken and the temperature allowed to rise to about  $40^\circ\text{C}$ . After keeping overnight, the products are distilled in steam, the first alcoholic runnings being collected apart. The mercaptan separates from the watery

distillate on standing and is tapped off; a further small quantity can be recovered by extraction with chloroform. It is, perhaps, preferable to keep the liquors loosely corked, when the mercaptan becomes oxidised to the disulphide which crystallises out and can be reduced back to mercaptan by the method described below. When the alcoholic runnings from the steam-distillation have accumulated they may be distilled, the distillate used to dissolve fresh sodium sulphide and the mercaptan in the residue driven over by steam.

The mercaptan produced by this method is contaminated to some extent with benzyl ethyl ether,<sup>1</sup> but can be obtained fairly pure by fractionation under reduced pressure. The yield never approaches the quantitative owing to the simultaneous formation of benzyl sulphide. This amounts to 16 per cent. of the benzyl chloride taken, even under the most favourable conditions. When the saturation with hydrogen sulphide is incomplete the yield of mercaptan falls, that of benzyl sulphide being proportionately increased, and if the saturation be slowly effected, oxidation of the sodium sulph-hydrate takes place and benzyl disulphide is produced by subsequent reaction with benzyl chloride.

In the course of some extended work on the sulphur compounds of benzyl, a large amount of benzyl disulphide had accumulated and a method was sought of utilising this as a source of the mercaptan. Many reducing agents were tried, but the best for the purpose was found to be iron filings in presence of acetic acid. The operation may be conveniently carried out as follows:—

100 grams of benzyl disulphide are dissolved in 350 c.c. of glacial acetic acid, 50 c.c. of water and 50 grams of iron filings are added in small quantities at a time, the addition occupying an hour. The materials are heated on the water bath and shaken at intervals and the heating and shaking continued for half an hour longer. The product is then

<sup>1</sup> See A. Forster, *Proceedings*, vol. xii., part 3, page 137.



distilled in steam; the yield of crude mercaptan amounts to 82 grams. A certain amount of hydrogen sulphide is formed during the reduction-process so that presumably the mercaptan is not quite pure. From the results of the reaction of this mercaptan, however, with sulphur dioxide (v. infra.) it would seem that the amount of impurity is not very great.

Mixtures of benzyl mono- and di-sulphide which are hardly resolvable by crystallisation may be treated in the same way as the pure disulphide. After distillation of the mercaptan in steam, the residue is filtered hot under pressure, and the liquid, unattacked monosulphide (M.P.  $49^{\circ}$ ), thus obtained free from unaltered filings, etc. The filtrate is cooled, shaken to granulate the monosulphide and the latter washed with water and dried. After one crystallisation from alcohol it is obtained in a perfectly pure condition. 330 grams of the mixed sulphides, treated in this manner, yielded 95 c.c. of mercaptan and 117 grams of pure benzyl sulphide.

For the preparation of benzyl trisulphide, the crude mercaptan, produced as above, may be used with advantage. It is mixed with an equal volume of glacial acetic acid, saturated simultaneously with hydrochloric acid and sulphur dioxide and allowed to stand until the lower liquid, which soon forms, ceases to grow at the expense of the upper. The product is then distilled in steam and the residue fractionated by crystallisation to separate the trisulphide from the disulphide which is formed in equal quantity.<sup>2</sup> The disulphide can be reduced again to mercaptan which serves for the production of more tri- and di-sulphides. In one experiment, 244 c.c. of crude mercaptan yielded 232 grams of mixed di- and tri-sulphides.

<sup>2</sup> See Smythe and Forster, *Chem. Soc. Trans.*, 1910, vol. xcvi., 1195.

## A NOTE ON THE PREPARATION OF ACRYLIC ESTER.

By F. G. TROBRIDGE, M.Sc., Ph.D.

[Read March 9th, 1912.]

As the treatment of acrylic acid with hydrochloric acid and alcohol, or the lead, silver, or potassium, salts of acrylic acid with methyl iodide does not yield acrylic ester, the only method at present available for the preparation of this ester is the reduction of dibromopropionic ester with zinc.

O. Röhm<sup>1</sup> allows the dibromopropionic ester to drop into a flask containing zinc and alcohol and separates the acrylic ester formed, by the method of Caspary and Tollens,<sup>2</sup> namely, by the addition of a 15 per cent. salt solution and subsequent distillation, the product obtained after several such operations being dried by calcium chloride. The author finds that the reduction in alcoholic solution starts readily and proceeds vigorously, but that the separation of the acrylic ester in a satisfactory yield by the above method is exceedingly difficult, much time being required and loss occasioned in freeing the ester from the last traces of alcohol. Much better results have been obtained by carrying out the reduction in ethereal solution by means of a moist zinc-copper couple. The reaction is somewhat difficult to start but once started proceeds vigorously the  $ZnBr_2$  remaining in solution. The yield is 80 per cent.

### EXPERIMENTAL.

Acrolein, prepared by the distillation of glycerine and boric acid,<sup>3</sup> is dissolved in ether, cooled, and the requisite

<sup>1</sup> *Ber.*, xxxiv., 573.

<sup>2</sup> *Ann. d. Chemie*, 167 (1872), 247.

<sup>3</sup> *Ber.*, xxxii., 1352.

quantity of bromine added to convert it into dibrompropionic aldehyde. This is oxidised with the calculated amount of fuming  $\text{HNO}_3$ , the product dried and esterified with alcohol and  $\text{HCl}$ . The dibrompropionic ester is fractionated in vacuum.

A moist  $\text{Zn-Cu}$  couple containing  $\text{Zn}$  in excess of the amount needed for the reduction is placed in a round-bottomed flask fitted with a reflux condenser, and covered with ether which must be absolutely free from alcohol. About half the dibrompropionic ester is added and the flask warmed and shaken till the reaction starts when the remainder of the ester is added. When the reaction has died down the liquid is poured off and shaken once with dil.  $\text{H}_2\text{SO}_4$  to remove the bulk of the zinc salts, the ethereal solution is again treated with the couple, after which it is shaken with very dilute  $\text{H}_2\text{SO}_4$  till free from  $\text{Zn}$  salts, dried by  $\text{CaCl}_2$  and distilled twice through a fractionating column. The ester obtained is perfectly pure.

## NOTE ON SOME PARA DERIVATIVES OF PHENYL- ACETIC ACID.

By S. ROBSON, B.Sc.

[Read March 7th, 1912.]

The object of this work was to find what are the products of nitration of parabromophenylacetic acid. Professor Bedson had obtained by fractional crystallization of the crude product of bromination of phenylacetic acid—a separation of pure parabromophenylacetic acid.\* In the present case the same product was obtained in the following way:—

Pure paranitrobenzylcyanide was obtained by the nitration of benzylcyanide and separated from the ortho compound by crystallization from glacial acetic acid. Its preparation is very simple, because nearly the whole product of nitration of benzyl cyanide is the para compound and the corresponding ortho compound is much more soluble in glacial acetic acid. Paranitrobenzylcyanide crystallises in large flat faintly yellow needles, M.F. 115° C., and yields on saponification with a mixture of sulphuric acid and water in equal proportions the corresponding phenyl acetic acid.

The paranitrophenylacetic acid so produced is identical with that obtained and described by Professor Bedson.

A determination in this compound of the "nitro group" by means of Limpricht's method, which consists of reducing the substance by means of an excess of stannous chloride and titrating back with iodine gave 25·79 per cent., whereas the calculated percentage for nitrophenylacetic acid is 25·41. Parabromophenylacetic acid was obtained from the pure paranitrobenzylcyanide by means of the Diazo Reaction—

$$\text{C}_6\text{H}_4\text{NO}_2\text{CH}_2\text{CN} \rightarrow \text{C}_6\text{H}_4\text{NH}_2\text{CH}_2\text{CN} \rightarrow \text{C}_6\text{H}_4\text{BrCH}_2\text{CN} \rightarrow \text{C}_6\text{H}_4\text{BrCH}_2\text{COOH}.$$

(2)
(1)
(2)

\* J.C.S., 1880.

The reduction was effected by means of stannous chloride. It was found best to use a considerably diluted solution for the diazotisation. On the addition of cuprous bromide in hydrobromic acid solution to the diazo compound the reaction is very vigorous and should be carried out in a large open vessel. The parabrombenzylbromide is best obtained by steam distillation, though partial hydrolysis takes place in the flask during the process and the parabromphenylacetic acid thus produced being non-volatile remains behind.

The cyanide thus obtained was saponified by means of sulphuric acid and water (alkalies must be avoided as they produce a brilliantly red coloured compound) and yielded a remarkably pure product melting at about  $112^{\circ}$  C., from which pure parabromphenylacetic acid melting at  $114^{\circ}$ - $115^{\circ}$  C. is readily obtained on further crystallisation. This compound is identical with that obtained by the fractional crystallisation of the mixed barium salts of the product of bromination of phenylacetic acid. From water it crystallises in long flat colourless needles, from glacial acetic acid in well formed rectangular plates. It yields on oxidation with potassium permanganate parabrombenzoic acid and an estimation of the bromine content by combustion with lime gave the percentage of bromine to be 37.63, whereas that calculated for bromphenylacetic acid is 37.20.

A further yield of a less pure product was obtained by extracting the contents of the flask with ether, washing the extract with alkali and reconverting into the acid again.

By a similar method to the above the para chlor and para iodo derivatives have been obtained and identified by their melting points and products of oxidation.

They are both similar in their reactions to the parabromphenylacetic acid. Crystallisation of the para chlor compound from glacial acetic acid yields rectangular plates corresponding very closely to those of the bromine compound.

The nitration of parabromphenylacetic acid yielded a product melting at  $110^{\circ}$ - $111^{\circ}$  C. and this on recrystallisation

yielded a substance melting at  $113^{\circ}$ – $114^{\circ}$  C. This compound crystallises from water in long flat yellowish needles, from glacial acetic acid in large yellow monoclinic prisms. It is much more soluble in water than either the parabrom or paranitro compounds and under certain conditions the halogen attached to the nucleus is reactive—the barium salt for example yielding with silver nitrate a precipitate of silver bromide.

On oxidation it yields parabrommetanitrobenzoic acid. An estimation of the “nitro” content and the bromine content yielded the following results:—

NO<sub>2</sub> estimated by Limpricht's method ... 17·37% .

Br estimated by combustion with lime ... 30·25% \*

The calculation for a bromnitrophenylacetic acid is 17·67 and 30·76 per cent. respectively.

From these considerations and from the general agreement in properties with those described by Professor Bedson this compound will be seen to be parabrommetanitrophenylacetic acid.\*

This is the only product of nitration of parabromphenylacetic acid.

The nitration of a mixture of para and ortho bromphenylacetic acids yields in addition to the above described compound two others designated by Professor Bedson  $\alpha$  and  $\beta$  bromnitrophenylacetic acids, and possibly another one. These compounds must have the bromine attached to the benzene nucleus in the ortho position. The compound has been obtained in the forms of large well shaped prisms having a definite melting point, but attempts to oxidise it to the corresponding benzoic acid and so determine its constitution have so far been unsuccessful.

In conclusion, I desire to thank Professor Bedson for his continued interest and valuable advice throughout the progress of this investigation.

\* J.C.S., 1880.

## ANALYSIS OF A FLORIDA CLAY.

By ARCHIBALD A. HALL, M.Sc., Ph.D.

[Read May 16th, 1912.]

In a previous paper in this *Journal* (vol. iv., pt. 2, page 83) an attempt was made to find out what differences in the composition of an underclay could be traced to the influence of the strata above it, more particularly what influence vegetation had on the production of our modern fire-clays. The present analysis is of interest in giving the analysis of a clay on which vegetation is now growing under conditions which approximate to those of the coal age.

The sample analysed was that of a clay subsoil underlying peat (15 feet thick) from Duval, County Florida, forming part of the great swamp of Florida. The sample was taken in April, 1911, and the analysis was done upon the air-dried sample. The methods of analysis were identical with those of the previous paper.

	I.	II.	ANALYSIS CALCULATED ON IGNITED CLAY.			
				III.	IV.	
Loss at 110° ...	6.00	2.00				
Loss on Ignition	12.47	8.10				
SiO <sub>2</sub> ...	55.56	56.00	SiO <sub>2</sub> ...	68.01	62.10	
Al <sub>2</sub> O <sub>3</sub> ...	19.23	29.08	Al <sub>2</sub> O <sub>3</sub> ...	23.54	32.20	
P <sub>2</sub> O <sub>5</sub> ...	.12	.028	P <sub>2</sub> O <sub>5</sub> ...	.14	0.03	
TiO <sub>2</sub> ...	.97	1.17	TiO <sub>2</sub> ...	1.18	1.29	
Fe <sub>2</sub> O <sub>3</sub> ...	3.50	1.70	Fe <sub>2</sub> O <sub>3</sub> ...	4.29	1.87	
CaO ...	.26	.88	CaO ...	.32	1.08	
MgO ...	—	.08	MgO ...	—	0.08	
K <sub>2</sub> O ...	1.11	1.08	K <sub>2</sub> O ...	1.35	1.19	
Na <sub>2</sub> O ...	.96	.15	Na <sub>2</sub> O ...	1.17	0.16	
CO <sub>2</sub> ...	—	—	CO <sub>2</sub> ...	—	—	
	<u>100.18</u>	<u>100.368</u>		<u>100.00</u>	<u>100.00</u>	

Analysis I. represents the analysis of the air-dried sample; III. calculated from this, is that of the ignited sample;

ii. and iv. represent the analyses of the air-dried and ignited samples of a typical underclay, lying under coal, and are placed here for comparative purposes.

The two analyses show great similarity in the main, that of the Florida clay showing a slightly greater percentage of silica and a lower percentage of alumina.

The most marked difference between the two clays is shown by the phosphorus and the iron; the Florida clay containing almost five times as much phosphorus as the clay from under the coal and twice as much iron.

The potassium is present in a slightly higher percentage in the Florida clay and the sodium in a considerably higher percentage. On examining the analysis of the two clays from the point of view of their capability of supporting vegetable life, it will be seen that the analyses of the Florida clay represents a poor soil, but one which is still capable of supporting vegetable life, whilst that of the clay from under the coal resembles a very deep subsoil from under a very poor surface soil, this difference is shown chiefly by the difference in the phosphorus and potassium content.



## THE RATE OF FERMENTATION AS MEASURED BY DIFFERENCE OF POTENTIAL.

Abstract of Paper by M. C. POTTER, Sc.D., M.A., F.L.S.

[Read March 12th, 1912.]

In a short paper read before this Society<sup>1</sup> I gave an account of some experiments showing that an electro-motive force is developed during the fermentation of sugar by yeast and also during the decomposition of various organic compounds by bacteria. These experiments were described in detail in the *Proceedings* of the Royal Society.<sup>2</sup>

The purpose of the present note is to show that an agreement exists between the rate of fermentation and this E.M.F. In determining the rate of fermentation the method of Slator<sup>3</sup> has been used with slight modification. The essential feature of this method is the measurement of the amount of CO<sub>2</sub> evolved in a given time by means of a mercurial manometer. The flask containing the fermenting liquid is connected with the mercurial manometer by means of a rubber tube, and vigorously shaken by the hand before each reading is made in order to liberate all the entangled gases.

In order to avoid any error which might be caused by a temperature difference due to handling during the shaking and also to maintain a constant temperature, the following modification was introduced. The flask containing the fermenting sugar was placed in a thermostat and oscillated continuously by means of a crank driven by an electric motor, the rubber tube from the flask passing through a

<sup>1</sup> *Proceedings* of the University of Durham Philosophical Society, vol. iii., 1910.

<sup>2</sup> *Proceedings* of the Royal Society, B., vol. lxxxiv., 1911.

<sup>3</sup> *Journal of the Chemical Society*, vol. lxxxix., 1906.

perforation in the door of the thermostat to the manometer. Readings of the amount of  $\text{CO}_2$  evolved during a given period of time—usually 5 minutes—gave an index of the rate of fermentation. Plotting these amounts of  $\text{CO}_2$  as ordinates with the intervals of time as abscissæ, a curve showing the progress of fermentation could be obtained.

It was found that the curves so produced agreed with the curves obtained by measuring the E.M.F., when the same amount of yeast was employed at the same temperature and concentration of sugar.

Thus the measurement of rate of fermentation by the development of the E.M.F. and by the evolution of  $\text{CO}_2$  are in close agreement, and this electrical method provides a ready means of determining the rate of fermentation.

Some experiments have also been undertaken to determine whether the rate of fermentation is influenced by the potential of the fermenting liquid. Two flasks, each containing the same amount of sugar solution and at the same temperature and concentration, were attached to the one axle and oscillated side by side in the thermostat. One flask was insulated by plates of ebonite fixed between it and the rotating axle, as well as by a short ebonite tube inserted in the rubber tube connected with the manometer. This insulation was found not to leak when tested with the electroscope. The other flask was not insulated; but could be earthed by means of a platinum electrode passing through a perforation in the stopper closing the neck of the flask. The rate of fermentation was found to be the same in both flasks within the limit of experimental error. Again, when the insulated flask was raised to 240 volts by connection with the electric mains the rate of fermentation was unaltered.

A further series of experiments designed to ascertain whether the  $\text{CO}_2$  as given off from fermentation carries an electric charge have given positive results, the gases escaping from fermentation discharging a gold leaf electroscope.

## BOULDERS COMMITTEE.

## REPORT No. 6.

## (a) Reported by G. WEYMAN, B.Sc.—

- (1) Boulder clay, Kenton Quarries. Greywacke (3); Porphyrite, Cheviots (2); Cheviot granite; Grey granite; Crystalline limestone; Quartz porphyry.
- (2) Gravel deposit, Horsebridge Head, Newbiggen. Flints (2); Quartzite; Schist (2); Quartz porphyry; Granite (3); Cheviot granite; Syenite (4); Mica porphyrite; Chert; Andesite; Breccia.
- (3) Boulder clay, Tynemouth. Greywacke; Granite (2); Syenite; Porphyrite; Microgranite.
- (4) Blue clay, Tynemouth. Volcanic series of Borrowdale; Granite.
- (5) Vicarage Burn, Bavington. Granite.

## (b) Reported by F. WALKER, B.Sc.—

- (1) Boulder clay, Armstrong Park, Heaton. Cheviot granite.
- (2) Standard Brick Works, Heaton. Basalt; Dolerite; Quartzite; Calcareous grit.
- (3) Boulder clay, Monkseaton. Granite; Syenite; Basalt; Volcanic series of Borrowdale.
- (4) Corbridge. Volcanic series of Borrowdale and granite.

## (c) Reported by Dr. WOOLACOTT—

Aycliffe Quarries. Resting on the limestone here is a blue stony clay, with sand, leafy clay, and yellow clay above. The surface is striated 30° W. of S. In the stony clay boulders of Threlkeld granite and volcanic series of Borrowdale occur.

## (d) Reported by F. WALKER, G. WEYMAN and Dr. WOOLACOTT—

From Armstrong Whitworth's New Shipyard, Walker-on-Tyne. Granite (Criffel); Several other granites; Syenite; Volcanic series of Borrowdale; Whin; Carboniferous limestone (several); Magnesian limestone; Brockram (Penrith) sandstone; Conglomerate (Tuedian?).

## (e) Reported by Dr. SMYTHE—

Striations observed on Whin Sill 300 yards east of Northside, Kirkwhelpington. Height 700 feet. Direction E.

Dr. Smythe makes the following further observations on the buried escarpment at Clousden Hill (see Report No. 5, p. 91, 1911):—

During October, 1911, a portion of the scarp face, about 15 feet high, was uncovered. The strike of the escarpment was 5° N. of W., and the slope of the face about 80°. The lowest visible portion, about 5 feet in height, was rough and showed no signs of glaciation. Above this, for 5 feet, the surface was strongly striated, the striæ dipping west at 10°. A broken patch intervened between the latter surface and the rounded edge of the escarpment, which, as mentioned before, was striated in a direction N.W.-S.E. The absence of glaciation near the foot of the escarpment, and the evidence of lateral displacement of ice to a depth of 10 feet below the edge, are points of some interest. The section was visible until January, 1912, when, owing to cessation of work, the garth became flooded.

## PAPERS READ BEFORE THE SOCIETY,

### SESSION 1911-1912.

#### GENERAL MEETINGS.

*November 24th*, 1910: "A Survey of the Girdle Stanes, Dumfriesshire,"\* by G. R. Goldsbrough, M.Sc.

*January 9th*, 1912: A discussion on "The Theory of Errors and its Application to Experimental Observations" was opened by S. H. Collins, M.Sc., and G. H. Thomson, M.Sc., Ph.D.

*May 17th*, 1912; "The Application of Scientific Method to the Study of History," by F. J. C. Hearnshaw, M.A.

#### SECTION A.

*November 24th*, 1911: "A Thermostat with Delicate Adjustment and Long Range,"\* by S. H. Collins, M.Sc., F.I.C. "A Water-sealed Constant Pressure Hydrogen Generator,"\* by S. H. Collins, M.Sc., F.I.C. "A Simple Gas Governor for Regulating the Flow of Gases,"\* by S. H. Collins, M.Sc., F.I.C.

*December 7th*, 1911: "Demonstration of Téclu's Method of Estimating the Calorific and Illuminating Power of Coal Gas," by P. P. Bedson, M.A., D.Sc. "A Modified Form of the Landsbergers Boiling-point Apparatus,"\* by J. H. Paterson, M.Sc. "On the best use of a Condenser as a Shunt to a Telephone Receiver in Wireless Telegraphy,"\* by H. Smith, B.Sc. "The Estimation of Mineral and Organic Acids in Vinegar,"\* by J. H. Paterson, M.Sc.

*February 1st*, 1912: "A Note on a Case of Stepwise Oxidation," by J. A. Smythe, D.Sc., Ph.D. "Pressure Displacement of Spectral Lines," by T. H. Havelock, M.A., D.Sc.

*February 15th*, 1912: "Cathode and Anode Reaction,"\* by J. H. Paterson, M.Sc.

*March 7th* 1912. "A Note on Some Para-derivatives of Phenyl Acetic Acid,"\* by S. Robson, B.Sc. "The Estimation of Hydroxyl Groups in Organic Compounds," by J. H. Paterson, M.Sc. "Analysis of Water-box Deposit from a Pit-shaft at Walker Colliery," by W. S. Oliver, B.Sc. "Note on the Preparation of Acrylic Ester,"\* by F. G. Trobridge, M.Sc., Ph.D.

*May 16th*, 1912: "Analysis of a Florida Clay,"\* by A. A. Hall, M.Sc., Ph.D. "On the Oxidation of some Organic Sulphur Compounds with Hydrogen Peroxide," by J. A. Smythe, D.Sc., Ph.D.

## SECTION B.

*December 5th, 1911:* "A Further Note on a Glaciated Escarpment,"\* by J. A. Smythe, D.Sc. "A Case of Megascopic Pseudostromatolism in the D<sub>5</sub> Coal-Measures of Northumberland,"\* by S. R. Haselhurst, M.Sc. "A Contrast in Contour," by D. Woolacott.

*December 11th, 1911:* "The Rate of Evolution of Hydrocyanic Acid from Linseed under Digestive Conditions,"\* by S. H. Collins, M.Sc. "A Preliminary Note on the Uniaxial Angites of the North of England Igneous Dykes,"\* by Mary K. Heslop, M.Sc.

*February 27th, 1912:* "Clovers under Cultivation," by D. A. Gilchrist, M.Sc. "The Felspars of Browney Colliery Sill as Compared with those of Tynemouth," by Mary K. Heslop, M.Sc. "Early Stages in the Development of the Vertebrate,"\* by Alexander Meek, M.Sc.

*March 12th, 1912:* "Rate of Fermentation as Measured by Difference of Potential,"\* by M. C. Potter, M.A., Sc.D.

## SECTION C.

*December 14th, 1911:* "Modern Theories of Number Considered as a Measure of Continuous Quantity,"\* by P. J. Heawood, M.A.

*March 14th, 1912:* "Orbital Motion in a Resisting Medium," by G. R. Goldsbrough, M.Sc.

## SECTION D.

*February 8th, 1912:* "Recent Pre-Historic Discoveries in Durham," by C. T. Trechman, B.Sc. "The Evolution of the Bronze Age, Spear, and Sword in Britain," by W. Parker Brewis, F.S.A.

*June 5th, 1912:* Members visited the ruins of Tynemouth Priory, which were described by Mr. W. H. Knowles, F.S.A., they then proceeded to Seaton Delaval where the Hall, designed by Sir John Vanbrough, architect of Blenheim and Castle Howard, was inspected.

## SECTION E.

*November 30th, 1911:* "Solution of some Problems in Statics by means of Virtual Displacements," by J. T. Dixon.

*December 6th, 1911:* "Calculations for Deflection of Steam Turbine Rotors,"\* by J. Morrow, D.Eng.

*February 14th, 1912:* "The Interdependence of the Naval Architect and Marine Engineer," by J. J. Welch, M.Sc.

*March 13th, 1912:* "The Stability of a Floating Triangular Prism," by F. H. Alexander.\*

\* Indicates papers published in the *Proceedings*.

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# UNIVERSITY OF DURHAM PHILOSOPHICAL SOCIETY

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## THE STRATIGRAPHY AND TECTONICS OF THE PERMIAN OF DURHAM (NORTHERN AREA).

By DAVID WOOLACOTT, D.Sc., F.G.S.

### I.—INTRODUCTION.

All geologists who have worked on the Permian of Northumberland and Durham have been impressed by the peculiarities of the Formation. Its great thickness of breccia for which no apparent general cause was assignable; its unique and complicated concretionary structures; the paucity and peculiar distribution of its fauna; and the very irregular deposition of its middle beds made it a most interesting and puzzling Formation, markedly different from others of the British Series. Although geologists at the end of the 18th century recognised that the Magnesian Limestone of Durham was later than, and had been deposited upon the Coal Measures, it was not until some years afterwards that mining engineers, acting upon the advice of Buddle, made borings through it and won the coal from under it. The first sinking through the limestone was started at Hetton (Angel or Blossom Pit) on the edge of the escarpment in 1820, and six years later one was begun at Monkwearmouth through the main mass of that rock.

The earliest papers that treat of the Permian of this area were published by Winch in 1817,<sup>1</sup> and Hutton in 1830;<sup>2</sup>

<sup>1</sup> *Trans. Geol. Soc.*, 1st ser., vol. iv., Part 1 (1817), p. 1.

<sup>2</sup> "Notes on the New Red Sandstone of the County of Durham below the Magnesian Limestone," *Trans. Nat. Hist. Soc. of Northumberland, etc.*, vol. i. (1831), pp. 60-74.

but no general description of the Permian rocks was given until 1835, when Sedgwick's classical memoir "On the geological relations and internal structure of the Magnesian Limestone"<sup>3</sup> appeared. In this work he refers to the great disturbing forces that have broken the rock into thousands of angular fragments, and suggests that the concretionary structures were produced shortly after the deposition of the beds. In the middle part of last century, although the work of Howse,<sup>4</sup> King,<sup>5</sup> and Kirkby<sup>6</sup> was chiefly directed towards a thorough palæontological examination of the limestone, they also each gave classifications of the Permian, and Howse drew an ideal section across the Permian outcrop.<sup>7</sup> In 1863 Daglish and Forster wrote a paper showing the relation of the Magnesian Limestone to the basin of the Coal Measures beneath,<sup>8</sup> and later, in 1881, the Geological Survey published solid and drift maps of the area by Howell, on which the outcrops of the Yellow Sands and the Magnesian Limestones are given.<sup>9</sup> Lebour in 1883 gave a description of the "Breccia Gashes,"<sup>10</sup> which are of common occurrence in the Middle and lower Upper Limestones, and during 1888 in an unpublished paper on "Some apparent unconformities in the North of England"<sup>11</sup> he suggested that certain disturbed beds in Frenchman's Bay might have been affected by the action of a thrust. About this time the same writer remarked of the Magnesian Limestone that "probably no other British rock offers so many types of structure displayed in a finer continuous section,"<sup>12</sup> In 1889 Howse drew up a catalogue

<sup>3</sup> *Trans. Geol. Soc.*, 2nd ser., vol. iii. (1835), p. 37.

<sup>4</sup> *Catalogue of the Permian Fossils of Northumberland and Durham*, 1848.

<sup>5</sup> "Monograph of the Permian Fossils," *Pal. Soc.*, 1849.

<sup>6</sup> *Q.J.G.S.*, xx., p. 345; *Trans. Tyneside Nat. Field Club*, vol. iv., Part 2, p. 212.

<sup>7</sup> *Annals and Magazine of Nat. Hist.*, Jan. 1857.

<sup>8</sup> *Trans. N. of Eng. Inst. of Min. Eng.*, vol. xiii. (1863-4), p. 205.

<sup>9</sup> 1 inch maps Geol. Survey, Nos. 105 S.E., 103 N.E. (New series, 21 and 27.)

<sup>10</sup> *Trans. N. of Eng. Inst. of Min. Eng.*, vol. xxiii. (1883), p. 165.

<sup>11</sup> Read before N. of Eng. Inst. Min. Eng.

<sup>12</sup> *Geology of Northumberland and Durham* (1886), p. 32.

of the Permian fossils in the Hancock Museum, Newcastle, in which he gave a general description of the Permian rocks, and suggested that the Yellow Sands were probably an æolian deposit.<sup>3</sup> In 1903 I published a detailed account of the Claxheugh section and attempted to give an explanation of its peculiarities,<sup>4</sup> which subsequent investigation has proved to be incorrect.<sup>5</sup> In the same year Lebour wrote a description of the Yellow Sands and Marl Slate<sup>6</sup> in which the present state of our knowledge of these deposits is fully stated. In 1909 it was shown from a study of the section between South Shields and Marsden that the Brecciated Beds occurred at different horizons in the Magnesian Limestone and were in this particular exposure a dynamic phenomenon produced by horizontal thrusting.<sup>7</sup> It afterwards appeared clear to me that the recognition of this thrusting gave possibly such a clue to the tectonics of the Permian as could not be otherwise obtained, and the work that has been done since on these rocks has been chiefly directed towards an elucidation of the deformations and other structural changes occurring in them. An attempt has also been made to map, classify<sup>8</sup> and describe the peculiarities notable in the deposition of the Magnesian Limestone. S. Rennie Haselhurst, M.Sc., who has made a detailed study of the Permian of the Northumberland area, has collaborated with me in describing this district, and C. T. Trechmann, B.Sc., has aided me in the preparation of the palæontological part of the paper.

<sup>3</sup> *Guide to Collection of Local Fossils in Nat. Hist. Museum, Newcastle*, 1889.

<sup>4</sup> *Nat. Hist. Trans. Northumberland, Durham and Newcastle-upon-Tyne*, vol. xiv., Part 2 (1903), p. 211.

<sup>5</sup> See references to Claxheugh section, pp. 295-296.

<sup>6</sup> *Trans. Inst. of Min. Eng.*, vol. 24 (1902-3), pp. 370-391.

<sup>7</sup> Woolacott, *Univ. of Durham Phil. Soc.*, Mem., No. 1, 1909.

<sup>8</sup> A preliminary note on the classification of the Permian of the North-East of England (B.A. Report, Winnipeg, 1909, p. 476), has been already published by me, but further study in the field has led to a better understanding of the stratigraphical peculiarities of the Permian series, especially as regards its Middle and Lower Upper beds. (See classification of the Magnesian Limestones, p. 252.)

## II.—TOPOGRAPHY.

(See FIGURES 5, 6 and 7)

The area of country dealt with forms a tract in East Durham measuring 12 miles from north to south, being about 2 miles broad at its northern extremity and widening, gradually at first, and then more markedly to  $5\frac{1}{2}$  miles at its southern limit. Its area is about  $48\frac{1}{2}$  square miles. On the west it is bounded by the Coal Measures lying along the base of the Permian escarpment, and includes the whole of the land lying between this scarp and the sea coast from South Shields to Hawthorn Dene. In Northumberland there are four small outliers of the Permian which are also included in the subject matter of this paper. In Durham the Magnesian Limestone forms an undulating area, resulting from the unequal durability of different parts of the limestone, and is quite distinct physiographically, as well as geographically, from the country to the north and west. On its western margin there is a distinct down-like escarpment rising in general some 200 feet above the Coal Measures. The general slope of the surface is towards the east. The escarpment reaches a maximum elevation at Warden Law (646 feet), where, however, the limestone is capped by a Kaim-like deposit of gravel and sand about one hundred and fifty feet thick, but at Penshaw Hill (456 feet), Hastings Hill (412 feet), Boldon Hills (307 feet) and Cleadon Hills (277 feet) the limestone forms the top of the escarpment. It is noteworthy that this elevated ridge is formed on Cleadon Hills of Upper Concretionary Limestone only, on Boldon Hills and Claxheugh of the Middle (Fossiliferous) and Lower Limestones, Marl Slate and Yellow Sands, while from Penshaw southwards it is entirely composed of the last three deposits. This portion of the country, where the regularly bedded Lower Limestone underlies a large area to the east of the escarpment, partakes of the nature of a dissected plateau. A second line of low rounded hills, which forms a distinct physiographical feature of the district, runs by High Barnes, Humbleton Hill (about

300 feet), Tunstall (373 feet), Dalton-le-Dale, Hesledon (418 feet) to Hawthorn, where it is partly cut through by the sea; it then turns inland and is continued southwards beyond the southern limits of the district surveyed, by Easington, west of Horden, etc. This ridge is formed of the fossiliferous unbedded type of the Middle Limestones, while a third minor ridge—a secondary escarpment—is produced by the outcrop of the Upper Concretionary Limestone on Fulwell Hill (230 feet), and Bilton or Building Hills, Mowbray Park, Sunderland (about 200 feet). The yellow bedded limestones of the Middle Permian and the breccias derived from them generally form low ground. The bed rock of the country is over large areas covered by superficial deposits which together form about three-fourths of the whole district. These comprise (1) clays, sands and gravels of direct glacial origin, (2) the Kaim-like mounds of sand and gravel of Warden Law and Grindon, (3) spreads of sand and gravel probably associated with the latter, (4) re-assorted boulder clay, (5) gravels and sands with marine shells (not found above the 150-foot contour), (6) a submerged deposit of vegetable remains. The escarpment and outcrop of the Permian is broken through by the Fulwell pre-glacial valley, now filled with superficial deposits; and since glacial times the gorge of the Wear has been cut through it.<sup>9</sup> Along the scarp on the west many indentations occur which have been cut by pre-glacial obsequent streams, while at the present day some westerly-flowing streams of this character run down the escarpment. Before the glacial period the surface of the country was deeply cut by dip streams which produced the wide “hopes.” These valleys were in general not entirely filled up by glacial deposits and the dip streams of the present-day flow along them in their upper courses, but in their lower they have cut deep gorge-like “denes.”

<sup>9</sup> Woolacott, “Superficial deposits and pre-glacial valleys of the North-umberland and Durham Coalfield, *Quart. Jour. Geo. Soc.*, vol. lxi. (Feb., 1905), p. 89.



The coast affords an almost continuous section of the Permian rocks (Fig. 9). It is in places rugged and picturesque, being rendered particularly so by the numerous stacks, arches and caves that occur along it. It is interesting to note that most of the stacks are entirely or partly composed of breccia.

### III.—THE COAL MEASURES FLOOR.

The Coal Measures lie in the form of a syncline under East Durham, the deepest part of the trough being beneath Sunderland. The Permian rocks thus rest unconformably on a denuded basin of Coal Measures<sup>10</sup> (see sections in Daglish and Foster's paper<sup>11</sup> and section, Fig. 1). It is, however, important to notice that the synclinal form of the Coal Measures in this area is a distinct accentuation of the general basin-shaped arrangement of the Northumberland and Durham coal-field, and as the Permian strata of north-east Durham are lying in a syncline with the highest limestones beneath the east of Sunderland, it would appear that the accentuation of the Coal Measures basin was at least in part post-Permian in origin. The thrusting and shattering to which the Magnesian Limestone has been subjected, and this secondary folding of the Coal Measures may have been produced at the same time.

The unconformity between the two formations is also clear in local limited exposures (*e.g.*, Tynemouth Cliff, Fig. 8) as the Carboniferous floor rises and falls beneath the Yellow Sands in a manner quite distinct from the general folding of the district. The dip of the Coal Measures is also sometimes seen to be distinct from that of the rocks above. The surface of the Coal Measures beneath the Permian is generally stained red. Sir R. J. Murchison and others looked upon these red beds as belonging to the Roth-todt-liegende,<sup>12</sup>

<sup>10</sup> In the south of Durham the unconformity is much more pronounced, the Permian there rests on the Carboniferous Limestone.

<sup>11</sup> *Op. jam. cit.*, p. 209.

<sup>12</sup> *Siluria* (1854), pp. 12 and 203.

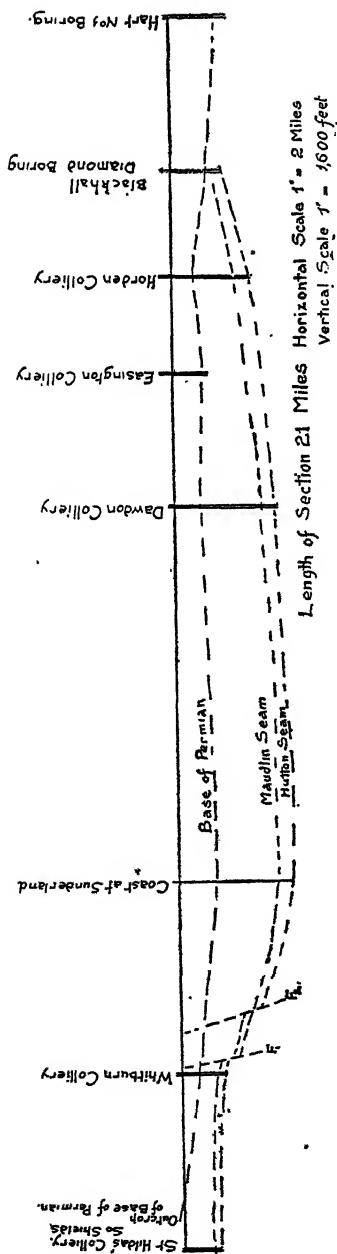


FIG. 1.—SECTION FROM SOUTH SHIELDS TO HART PARALLEL TO DURHAM COAST, SHOWING THE LIE OF THE COAL MEASURES AND OF THE BASE OF THE PERMIAN BENEATH EAST DURHAM.

$F_1$  and  $F_2$  are faults proved in Whitburn Colliery workings. The throw in the Coal Measures of  $F_1$  at one part is 240 feet, and of  $F_2$  is 132 feet. Both of these faults have a much smaller throw in the Permian. Many other faults are omitted as they do not affect the general lie of the beds.

but that they are the reddened edges of the Coal Measures is now accepted. Daglish and Foster suggested that the staining had been produced by the weathering of the Carboniferous prior to the deposition of the Permian,<sup>3</sup> while Professor Lebour writes that "the red colour has probably been obtained at the expense of the Yellow Sands, which were very likely once red too."<sup>4</sup> It may be that the iron existed in the Yellow Sands in the ferrous state, and has been transferred, hydrated and oxidised, into the Coal Measures beneath.

It is certain that a very large number of the faults—some of them of considerable throw—in the Coal Measures do not cut the Permian rocks, while some have a much greater throw in the lower than in the upper beds. The Ninety Fathom "Dyke" is of the latter class. On the other hand, many of the disturbances—thrust planes, local folds, fissures, etc.—occurring in the Permian strata do not reach the strata beneath.

Considerable horizontal movements have taken place in the Coal Measures, resulting in the disturbance of the softer beds (shales, etc.) between the more resistant sandstone masses. The former have been fractured, tilted, folded, and cleaved, and certain of the sandy shales have had secondary structures (pseudo-stromatolite, etc.) developed in them produced by the shearing of the mass.<sup>5</sup> This thrusting in the Coal Measures which can be best seen along the coast between Whitley and Tynemouth appears to have been produced by the same forces that produced the crush breccias in the Permian rocks above.

<sup>3</sup> *Op. jam. cit.* pp. 209-211.

<sup>4</sup> *Geology of Northumberland and Durham* (1886), p. 39.

<sup>5</sup> Lebour and Smythe, "On a case of thrust and unconformity in the Coal Measures of Northumberland," *Quart. Journ. Geol. Soc.*, vol. lxii. (1906), p. 530. S. R. Haselhurst, "A case of megascopic pseudo-stromatolite in the Coal Measures of Northumberland," *Univ. Durham. Phil. Soc.*, vol. iv. (1912), Part 3, p. 162.

## IV.—DIVISIONS OF THE PERMIAN.

It does not form part of the purpose of this paper to enter into a discussion of the conditions under which the Permian rocks were deposited, but it would seem essential for an understanding of the divisions of the formation that the general conditions should be briefly stated. The Yellow Sands may have been originally a delta formation—as suggested by the late Professor Green<sup>6</sup>—derived from older rocks lying to the west and north-west, but there can be little doubt that they were reassorted and redistributed by wind.<sup>7</sup> The sea—in which the later Permian rocks were accumulated and which was already in part cut off from the main ocean—gradually encroached on these sands, redepositing their upper parts in regular layers, and then tranquilly laying down upon them a laminated mud—the Marl Slate. Professor Lebour has suggested that this bed was deposited in a chain of shallow lagoons lying along the edge of the inland sea,<sup>8</sup> and Howse that it was spread over low-lying estuaries.<sup>9</sup> The remarkable persistence of this very thin deposit is, however, rather difficult to explain on either of these hypotheses. Meanwhile, evaporation from and concentration of the dissolved salts in the inland sea was taking place so that conditions were brought about which led to the gradual deposition of these salts. This sea was almost entirely cut off from the Permian waters of the West of England by the Pennine anticlinal, but may have extended across from the North of England into Eastern Germany and

<sup>6</sup> *Geol. Mag.*, vol. ix. (1872), p. 101.

<sup>7</sup> Howse. *Guide to Collection of Local Fossils in the Museum of Nat. Hist., Newcastle* (1889), p. 26.

<sup>8</sup> *Trans. Inst. of Min. Eng.*, vol. xxiv. (1902-3), p. 381.

<sup>9</sup> *Op. jam. cit.*, p 22.

Russia. In Thuringia the Zechstein series is very similar in general characters to that of the Magnesian Limestone of Durham, and the conditions of deposition appear to have been very much the same; but the areas were probably more or less isolated centres of deposition towards the end of the Permian period. There is, perhaps, no need to suppose that abnormal magnesian and other springs were running into the sea, as some writers have suggested,<sup>10</sup> although a large amount of dissolved matter would be constantly brought in by rivers and streams. The first beds to be laid down were a series of limestones forming the strata now known as the Magnesian Limestone, which have certainly undergone much alteration since they were deposited. The fauna living in this sea were compared with its progenitors of the Carboniferous Limestone period remarkably diminished in its number of genera and species, and in the size of its individuals. Another interesting feature of it is that in the area exposed in Durham brachiopods, polyzoa, corals, encrinites, and cephalopods do not pass beyond the top of the fossiliferous division of the Middle Limestone, while the number of genera of gastropoda and lamellibranchs persisting into the Upper beds is remarkably few. It is also peculiar that the highly fossiliferous Middle Limestone is amongst the most highly magnesian part of the series. Before a thorough knowledge of the conditions under which the Magnesian Limestone of Durham was deposited is obtained, we must know more regarding the conditions of solubility of calcium and magnesium carbonate in water and in carbonic acid in presence of one another and of such other salts as must have existed in a more or less isolated sea; indeed, such a knowledge of these conditions, as far as they can be obtained, similar to that which Van't Hoff has worked

<sup>10</sup> Green suggested that mineral springs produced by volcanic activity, furnished the mineral salts.

out for the salts of the Stassfurt area.<sup>11</sup> That the magnesium salts were present in the Permian sea seems to be certain; and that the magnesia was introduced into the limestone during or immediately after deposition by the action of magnesium chloride on the calcium carbonate is most probable. Since deposition, however, great changes in the amount of the calcium and magnesium carbonate present in certain beds at any particular part have taken place. In the great majority of cases the magnesium carbonate has been leached out, but sometimes both carbonates have been removed. These dissolved substances may conceivably be redeposited in the rock again or may be carried away (see formation of concretionary structures, page 268, and of cellular structures, page 305). While studying the Magnesian Limestone in the field special attention was paid to the cellular structures to see if they afforded any evidence of having been produced by a decrease in volume, such as would occur if extreme dolomitisation had taken place, but it was found that (see page 305) they seem to have been in most cases produced by the removal of the magnesium carbonate (or of both carbonates) and not by its introduction into the rock.

After the limestones had been formed, a series of marls, marly sandstones, and thin Fossiliferous Magnesian Limestones, with lenticular beds of salt, anhydrite<sup>3</sup> and gypsum were deposited. Whether evaporation went on in the sea in which the Permian rocks of Durham were formed so that the more soluble salts of calcium, magnesium, sodium and potassium were laid down (similar to the deposits of the Stassfurt area) we have no means of telling.<sup>3</sup>

<sup>11</sup> There is a summary of this work in *Data of Geo-Chemistry*, Clarke, *U.S. Geol. Sur. Bulletin* 330 (1908), pp. 176-182.

<sup>3</sup> For a description of the conditions governing the deposition of salts in an inland sea, reference may be made to "The data of geochemistry," *op. jam. cit.*, pp. 137-8, and for a summary of our knowledge of dolomites and Magnesian Limestones, *ibid.*, pp. 481-490.

FIG. 2.—THE LITHOLOGICAL DIVISIONS OF THE PERMIAN OF THE NORTHERN AREA.



UPPER RED BEDS WITH SALT (occur only in the south of Durham).

The limestones are overlaid in the south of Durham by a series of marls, etc., with fossiliferous magnesian limestones and beds of salt, anhydrite and gypsum. Thickness 300 feet

### UPPER LIMESTONES.

Upper yellow limestone of Roker and Sunderland Docks. A few species of fossils occur. Thickness 100 feet. This is the highest bed exposed in north of Durham.

The concretionary limestone of Cleadon, Fulwell and Building Hills, of coast from Marsden Bay to Parson's Rock, Roker, of Hendon, etc. A series of concretionary (greystones), compact (bluestones and whitestone) and crystalline limestones, and marls. Fossiliferous in places, but few species. Thickness 150 to 250 feet.

The FLEXIBLE LIMESTONE of Marsden, Hendon, etc. Thickness about 12 feet.

**MIDDLE LIMESTONES**, *a* unbedded (as a rule) highly fossiliferous (generally) limestone. Thinning rapidly ou east. Seen at Boldon Hills, Claxheugh, Humbleton and Tunstall Hills, Ryhope, Daltou-le-Dale, Fox Cover Quarry, etc. Often brecciated. Thickness up to 300 feet. \*

*b* Bedded yellow unfossiliferous limestones of coast, north end of Marsden Bay Hendon to Seaham Harbour, and south of same place to Chourndon Point. On banks of Wear above Sunderland Bridge, etc. Often highly brecciated. Thickness up to 200 feet.

## LOWER LIMESTONE

The regularly bedded limestone of Cullercoats, Tynemouth, Frenchman's Bay, Claxheugh, Houghton and escarpment south of Wear. Fossiliferous locally. Thickness up to 250 feet.

MARL SLATE. 3 feet.

**The YELLOW SANDS.** Thickness variable up to 150 feet.

## Unconformity

### COAL MEASURES.

## V.—THE YELLOW SANDS.

The Yellow Sands rest on the denuded edges of the Coal Measures, and underlies nearly the whole of the calcareous facies of the Permian of the district, apparently filling up the hollows in the floor on which it rests. Its thickness varies from 0 to 150 feet. Beyond the district under examination it appears to thin irregularly but continuously towards the south-west of Durham. In Northumberland it occurs in four outliers of the main Permian mass (1) at

\* In the south this limestone appears under another facies on the west, the unbedded fossiliferous rocks changing into bedded rocks with a very limited fauna. There are thus 3 distinct types of the Middle division.

DIVISIONS OF THE PERMIAN AND CORRELATION WITH OTHER AUTHOR'S DIVISIONS.

Divisions.	Places where typically developed.	Proposed Topographical Names	Sedgwick (1833).	King (1849).	Howse (1853).	Howse and Kirby (1893).	Howse (1899).
Upper Magnesian Limestone	Upper red beds with thin limestones, salt, etc.	The Middlesbrough red beds with salt.	Marls, etc., noted further south.	..	..	..	Brotherton Beds (equivalent to) Red Marl.
	The Upper Yellow Limestone.	Roker Foreshore, Sunderland.	The great middle deposit of Yellow Magnesian Limestone including Laminated, Earthy, irregular and	Crystalline, Earthy, Compact and Oolitic Limestones.	Upper Yellow Limestone.	Upper Limestone.	Upper thin-bedded Limestone.
	The Concretionary Limestone.	Marsden and Fulwell Quarries, Cleadon and Building Hills, Coast from Marsden to Roker.	The Fulwell Limestone.		Botryoidal Limestone.		Botryoidal Conglobated or Ball Limestone.
	The Flexible Limestone.	Marsden Bay, Hendon.	...	...	...	...	...
Middle * Magnesian Limestone	(a) The Unbedded Fossiliferous Middle Limestone.	(a) Tunstall, Humbleton, and Boldon Hills.	(a) The Tunstall Limestone.	Fossiliferous and Brecciated and pseudo-Brecciated Limestone.	Shell and Cellular Limestone.	Shell and Cellular Limestone.	Concretionary Shell and Cellular.
	(b) The Bedded Middle Limestone.	(b) North End of Marsden Bay. Coast from Bieldon Hills. Claxheugh, Hendon to Fox Cover Seabam Quarry.	(b) The Marsden Limestone.				
Lower Magnesian Limestone	The Lower regularly-bedded Limestone.	Houghton Quarries, High Down's Quarry, Frenchman's Bay, Boldon Hills, Cullercoats Bay.	The Houghton Limestone.	Compact Limestone.	Compact Limestone and conglomerate.	Lower Limestone.	Lower Limestone.
...	Marl Slate.	Cullercoats Bay, Lynemouth, and along escarpment in Durham.		Marl Slate.			
...	The Yellow Sands.	Claxheugh, Cullercoats Bay, Tynemouth, High Down's Quarry.	Lower Red Sandstone.	Various <sup>2</sup> Coloured Sandstones.	...	Lower <sup>3</sup> Red Sandstone.	Yellow Sand.

Note.—The correlations of the Middle and Upper Limestones are, owing to reasons explained in the paper, not exact.

\* I have already proposed in a preliminary note on the classification of the Permian of N. E. England B. A. report, 1909, p. 476, the term Claxheugh Limestone as a topographical name for this bed; but its development at Tunstall Hill gives a better exposure of its thickness and general characteristics.

<sup>2</sup> These included a part of the Upper Red Beds of the Coal Measures.

<sup>3</sup> There are three distinct facies of this division (see page 262.)



The Permian deposits of Durham may be correlated with those on the Continent as follows :—

Divisions.	Development on Continent.			Development in Durham.
Upper Permian (Thuringian).	Oberer.	Oberer Letten mit gyps.	Thon. Anhydrit. Gyps.	Red beds with Fossiliferous Magnesian Limestone, salt. anhydrite, etc.
		Plattendolomit.	Steinsalz. Kalisalz.	
		Unterer Letten mit gyps.	U.s.w. (Stassfurt).	
	Mittlerer.	Stinkschiefer.		The Upper Limestones.
		Mittlerer Dolomit und Rauchwacke. Anhydrit (älterer gyps).		Middle Bedded Unfossiliferous Limestones (often brecciated).
Middle Permian (Saxonian).	Unterer.	Zechstein mit Productus Horridus.		Middle Fossiliferous Limestone } With Productus Horridus.
		Kupferschiefer.		Lower Bedded Limestone
		Zechstein conglomerat (nur local entwickelt).		Marl Slate.
Middle Permian (Saxonian).	Weissliegendes.			The Yellow Sands up to 150 feet.
	Rothliegendes (500-2,000 metres).			
Lower Permian (Artinskian).	Artinsk group of sandstones, conglomerates, shales, marls, limestones and dolomites.			The Yellow Sands?
The Magnesian Limestone Group, up to 1,100 feet.				

(\*) The divisions of the Zechstein are adopted from Lethaea Geognostica. See Dyas von Fritz Frech (1901), p. 562.

The Magnesian Limestone Group, up to 1,100 feet.

Closing Hill near Killingworth (now no longer exposed), (2) at Hartley, (3) beneath the Magnesian Limestone and Marl Slate at Cullercoats, and (4) in the same position at Tynemouth. In Durham its top can be seen in Frenchman's Bay, and it can be followed more or less continuously along the escarpment to the south of the area. Its course can be traced by the line of gently sloping country at the base of the Magnesian Limestone ridge, or by the line of springs that occurs along part of its outcrop. Howse and some other geologists classed these beds with the underlying red beds of the Coal Measures, but there can be little doubt that the view stated by Professor Lebour in the following words is the correct one: "The Yellow Sands are everywhere unconformable on the beds beneath them, and therefore, though no fossils have been found in them, there can be no hesitation in classing them with the Permian and not with the Coal Measures."<sup>7</sup>

The characteristics of this deposit are as follows:—(1) It is generally very false-bedded, but the grains are more regularly arranged near the top of the deposit, (2) it is very seldom in distinct layers, (3) the grains composing it are generally quartz, but there is a considerable admixture of other minerals and rock fragments; felspar, mica, garnet, zircon, rutile, tourmaline and other substances occur in it. R. C. Burton and S. R. Haselhurst have studied the minerals of higher specific gravity in these beds. (4) The larger fragments composing it are rounded, but the smaller grains are generally angular; (5) there has been little sorting out of the grains, large and small being intermingled. (6) The lines in which the particles are arranged are curved, and they exhibit a feature which is possibly more characteristic of æolian than of water-formed false-bedded deposits, in that the lines along which the grains in any false-bedded mass are arranged curve round so as to become tangential to the top of the mass beneath. (7) It is generally yellow

<sup>7</sup> *Geology of Northumberland and Durham* (1886), p. 38.

along the outcrop, but is sometimes variegated from black to yellow. A black variety in the Down Hill Sand Pit was proved to be coloured by manganese dioxide. At one point in Houghton Quarry its top is silvery and the component particles angular. The name Yellow Sands is, however, somewhat of a misnomer, for in sinkings, where it has not been weathered, it is of a bluish, greenish or greyish colour.<sup>8</sup> (8) It is very irregularly cemented, being sometimes hard and compact, at others soft and friable. It is generally very strongly cemented beneath the Marl Slate and along veins. The cementing material is generally carbonate of lime, and it is often concentrated round points, so that a knobbly appearance is produced on weathering. (9) It is sometimes cut by fissures, and especially so parallel to post-Permian faults, or where it has been affected by thrusting. Cullercoats Bay and Claxheugh are the two most fissured areas.<sup>9</sup> (10) The passage into the argillaceous calcareous beds above is generally marked by the appearance of a bed of calcareous clay followed by the thinly-bedded Marl Slate, but at Cullercoats and Tynemouth the change is not so abrupt,<sup>10</sup> beds of sand being intercalated in the Lower Limestone at the former place, and a band of calcareous sandstone and conglomerate lying above it at the latter. (12) It is a water-bearing horizon. Browell and Kirkby<sup>11</sup> state that 1 cubic foot of the Yellow Sands absorbs 6 to 12 lbs. of water. Professor Lebour showed that it was being internally denuded by the springs that run from its base

<sup>8</sup> In the Dawdon sinking it is described as follows:—Blue grey sand 75 ft., brown grey sand 17 ft. 4 in., very hard girdle (greystone), 1 ft. See paper by E. S. Wood on "Dawdon Sinking," *Trans. Inst. Min. Eng.*, vol. xxxii. (1906-7), p. 573; and in Horden Sinking, blue grey sand 96 ft. 10 inch. See J. J. Prest on "Shaft Sinking at Horden Colliery," *Proc. Inst. Civ. Eng.*, vol. clxxii. (1907-8), pt. iii., plate 2, fig. 2, and account of strata sunk through at Horden.

<sup>9</sup> See description of Permian of Northumberland, p. 308.

<sup>10</sup> *Ibid.*

<sup>11</sup> Browell and Kirkby, "On the Chemical Composition of the Magnesian Limestone and Associated Beds of Durham," *Nat. Hist. Trans. Northumberland and Durham*, vol. i. pt. ii. (1866), p. 204.



*Photo by D. Woolacott.*

FIG. 3. -- YELLOW SANDS 1, MARL SLATE 2, LOWER LIMESTONE 3, AND FOSSILIFEROUS LIMESTONE 4.

The Marl Slate and Lower Limestone are absent from far end of exposure having been thrust out of position. The house in distance stands on Coal Measures against which the Permian is faulted. The Lower Limestone is thrust over the Fossiliferous at the west end of the railway cutting behind the escarpment. Claxheugh, near Sunderland.



*Photo by Godfrey Bingley.*

FIG. 4. -- YELLOW SANDS SHOWING FALSE-BEDDING.

The curving of the lines of bedding is shown, and the weathering is characteristic. -- Claxheugh, near Sunderland.



carrying away continuously small quantities of it.<sup>2</sup> This action can be observed at the present time along the line of springs between Houghton-le-Spring and Warden Law. The continuous pumping of water from it and the superincumbent limestone also abstracts material mechanically from these deposits. (13) No fossils have ever been found in the Yellow Sands.

These sands appear to have been derived from an area lying to the north and west in which some metamorphic rocks were exposed.<sup>3</sup> They were at first an æolian deposit of sand dunes on the edge of the Permian sea, and their upper parts were later washed up and deposited under water.

## VI.—THE LITHOLOGICAL DIVISIONS OF THE MAGNESIAN LIMESTONE.

No satisfactory classification of the Magnesian Limestone of this part of England has yet been given, because the brecciated beds have always been supposed to mark a particular horizon, which is not the case.<sup>4</sup> Moreover, a bed may be brecciated in one locality and not in another, and since the shattering of the strata undoubtedly occurred after deposition, the breccias obviously could not be used as a basis of stratigraphical classification even if they were confined to some special division. The concretionary structure has also been made to play the part of a zonal characteristic. It is, in truth, much more definite in the horizon which it affects than the brecciated limestone, but if, as there is every reason to believe, it is like the latter a secondary structure, it is equally unsuitable as a stratigraphical criterion. Besides, concretions more or less incipient occur in all the divisions of the limestone, though the more complex forms are to be found in the so-called Concretionary

<sup>2</sup> "The Marl Slate and Yellow Sands of Northumberland and Durham," *Trans. Inst., Min. Eng.*, vol. xxix. (1903), p. 377.

<sup>3</sup> *E.g.*, Central Scotland.

<sup>4</sup> See Memoir on Marsden, *op. jam. cit.*, sections 6 and 8.

Limestone of the Upper division only. It must be noted, however, that this subdivision, notwithstanding its name, is by no means concretionary throughout. As the Flexible Limestone occurs on a definite horizon and is lithologically and palæontologically peculiar (see p. 266) I have taken this bed as a line of separation between the Middle and the Upper Limestones, thus doing away with any dependence of the divisions on secondary structures.

The most important stratigraphical peculiarities in the Magnesian Limestone are, first, the thickening of the Lower Limestone southwards in the area discussed, and then thinning towards the south of Durham; second, the long ridge-like mass of unbedded (as a rule) Fossiliferous (generally) Limestone of the Middle division, which thins out rapidly eastwards and increases in thickness along the ridge to the south, and third the thickening of the Concretionary Limestone to the north in the Marsden area. The recognition of these changes in the thickness of deposition in these divisions is most important for a correct knowledge of Permian stratigraphy, and for an appreciation of the dependence of the contour of the area on its geology. The thickening of the Lower Limestone southwards and of the Concretionary northwards brings about an equivalence of deposition within the area.

Although the maximum thickness of limestone within the area when the total thickness of each division is placed in a vertical column (see page 252) totals up to about 800 feet, yet owing to the irregular deposition of the beds a boring through all the divisions, which could be obtained at the mouth of the Wear at Sunderland would probably pass through only about 500 to 600 feet of rock. In the south of Durham the greatest thickness of limestone proved by boring is 878 feet.<sup>5</sup> There is an increase in total deposition to the south.

<sup>5</sup> If the beds were dipping this may be greater than the true thickness.





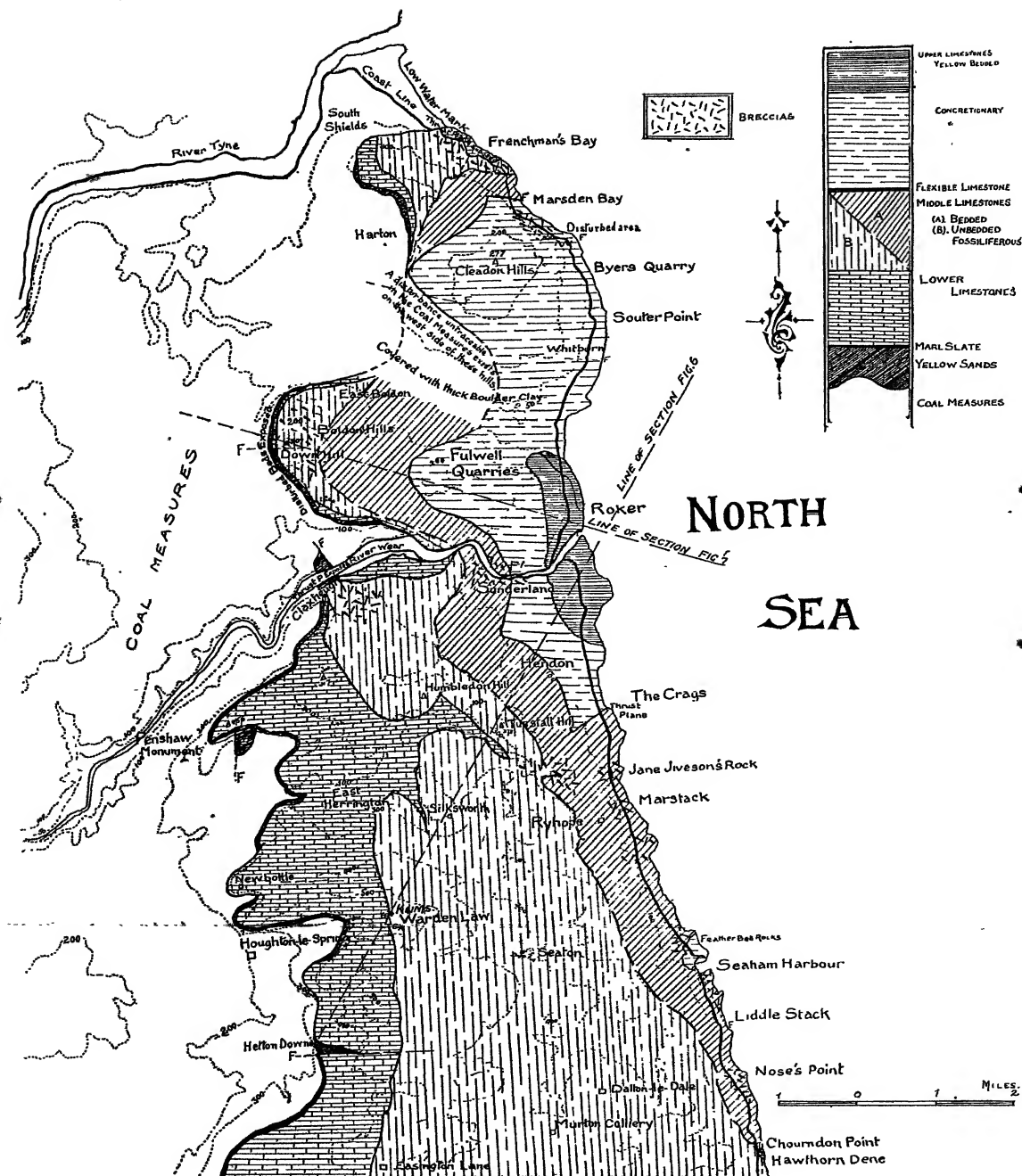


FIG. 5.—MAP SHOWING THE OUTCROPS OF THE CHIEF DIVISIONS OF THE PERMIAN AS THEY OCCUR IN NORTH-EAST DURHAM.—*D. Woolacott.*

Much of the country is covered by boulder clay and the junctions between the different divisions are generally obscured. Minor faults, etc., are omitted.



Grains of quartz often rounded, and of other minerals can be found in the limestone at many horizons;<sup>6</sup> and sometimes thin distinct local beds of sand, generally associated with marl, occur. One of these, which is micaceous, forms a distinct bed lying on the eastern flanks of the Middle Fossiliferous Limestone at Tunstall Hill, and thus separates this bed from the Middle bedded (here brecciated) Limestone. These arenaceous deposits total up to a very small part (much less than 1 per cent.) of the calcareous beds.

In composition the Magnesian Limestone is very variable. Leaving out the Marl Slate which is a transition deposit, and speaking only of the limestone proper, the amount of calcium carbonate varies from 99 to 38 per cent., and the magnesium carbonate from less than 1 to 50.<sup>7</sup> It is never a true dolomite while it sometimes approximates to a pure limestone. The amount of silica, alumina and oxide of iron is also very variable, reaching as much as 30 per cent. in the more marly varieties, and being less than 1 in the purer limestones.<sup>8</sup> Arborescent manganese dioxide is of frequent occurrence.

Kirkby and Browell showed that in general it may be said that the earthy marls and friable yellow limestones are the most magnesian, the compact (softer varieties) non-crystalline and non-concretionary are intermediate in character, while the crystalline and concretionary beds contain still less magnesia.

The purest limestones are, however, certain non-concretionary crystalline, compact beds (bluestones) in the Concretionary Series.<sup>9</sup> Colour is a less reliable indication

<sup>6</sup> C. T. Trechmann, B.Sc., has studied a limestone residue from these beds at Hartlepool, and found in it: (1) Quartz grains, some with idiomorphic outlines, (2) iron pyrites, (3) highly refracting grains resembling zircons, (4) a dichroic mineral, possibly tourmaline.

<sup>7</sup> From analyses in Browell and Kirkby's paper and from other analyses.

<sup>8</sup> Some shaly partings in the Lower Limestone contained 80 per cent. of these substances.

<sup>9</sup> See page 269.

of composition than texture, though generally the light yellow beds are most magnesian, and those of darker colour (brown and grey) are the most calcareous.<sup>10</sup>

As regards the distribution of the character of bedding, texture, colour, etc., it may be said that the Lower Limestone and Upper Yellow are the most evenly bedded and least changeable in colour and texture, the Middle and part of the lower Upper (Marsden area) most variable in bedding on a large scale, while the texture, colour, and stratigraphical peculiarities vary most in the Concretionary Limestone. All the divisions are very variable in composition, but it may be noted that the Upper Concretionary changes as a rule from bed to bed, while the others more often vary from locality to locality.

## VII.—MARL SLATE.

This thinly laminated arenaceous, argillaceous and calcareous bed is traceable above the Yellow Sands throughout the area. It is generally overlain by limestone, but on Tynemouth Cliff there is a calcareous sandstone and conglomerate 6 feet thick between it and the limestone, and in Cullercoats Bay some thin beds of sand are intercalated above it in the lower beds of the limestone. Sometimes thin bands of a Marl Slate type are interbedded with the lower calcareous strata. At its base there is often a thin bed of soft clay, and while its bottom layers are argillaceous, yet nearer the top it becomes an impure limestone. Along its outcrop in Durham it is generally yellowish brown, but in some exposures it is grey and black, and in sinkings it is of a dark colour. Within the district it is never more than three feet thick. It thins out in the south-west of Durham. Analyses of the Marl Slate vary considerably, the following are some from Kirkby and Browell's paper:—<sup>11</sup>

<sup>10</sup> Browell and Kirkby.

<sup>11</sup> *Op. jam. cit.*





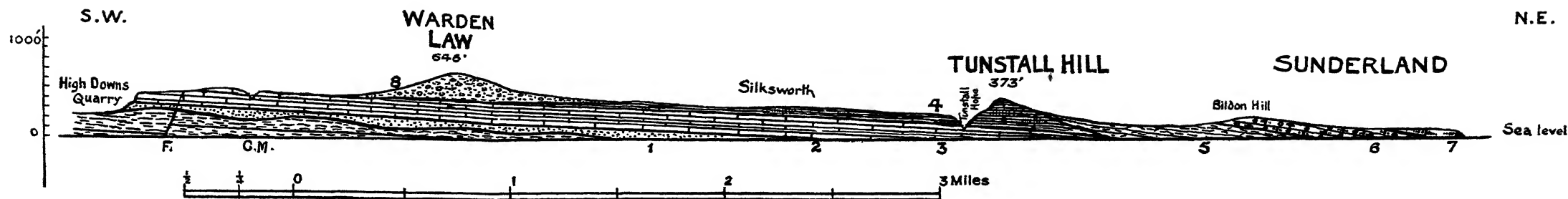


FIG. 6.—GENERAL SECTION ACROSS THE PERMIAN OUTCROP FROM HIGH DOWNS QUARRY, HETTON, TO SUNDERLAND SHOWING THE SEQUENCE IN THE NORTH OF DURHAM.—*D. Woolacott.*

C.M. Coal Measures.

1. Yellow Sands.

2. Marl Slate.

3. Lower Regularly-bedded Limestone seen in Hetton Downs Quarry and (the top beds) in Tunstall Hope. This bed thickens eastward.

4 and 5. Middle Magnesian Limestones. 4 are unbedded, highly fossiliferous rocks, passing westwards into bedded rocks with a limited fauna, and thinning rapidly on eastern margin and replaced by bedded yellow rocks, often highly brecciated. (5) On the south-eastern flanks of Tunstall Hill (near Ryhope Colliery) there is a bed of marly micaceous sand between 4 and 5.

6. The Upper Concretionary Limestone.

7. Upper Bedded Yellow Limestone of Roker.

8. Kaim-like mass of sand and gravel.

The other superficial deposits are omitted. The boulder clay is most thickly distributed over 5. Disturbances in the limestone (faults, etc.) are omitted as they do not alter the general sequence.

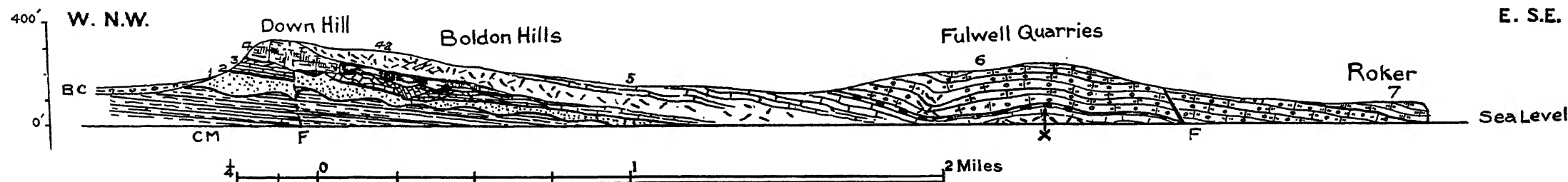


FIG. 7.—SECTION ACROSS THE PERMIAN OUTCROP FROM DOWN HILL, WEST BOLDON, TO ROKER, NEAR SUNDERLAND,—*D. Woolacott.*

C.M. Coal Measures.

1. Yellow Sands.

2. Marl Slate.

3. Highly disturbed Lower Limestone. The section of this rock endeavours to give a general impression of the exposures seen along the flanks of Boldon Hills—at base of Down Hill and near Hylton Castle. This disturbance is on the same horizon as the sheared and tilted beds above the thrust plane in Frenchman's Bay.

4. Fossiliferous Unbedded Middle Limestone, often brecciated.

4A. Breccia (probably a brecciated part of the Fossiliferous Limestone with fossils—if any were originally present—obliterated)

5. Bedded Yellow Middle Limestone, which are highly brecciated along the banks of the Wear west of Sunderland Bridge corresponding to breccias shown immediately above letter X. The brecciated beds were recorded by Kirkby as occurring beneath the Upper Limestone in Fulwell Quarries.

X. Fish bed of Fulwell, not exposed along surface but worked into at base of the Concretionary Limestone. This bed corresponds in position with the Flexible Limestone.

6. Upper Concretionary Limestone with the most varied development of the concretionary structures and occasional fish remains.

7. Upper Yellow Limestone of Roker.

F. Faults.

The section is partly obscured by boulder clay (B.C.) which is only shown above the Coal Measures.





	<i>Ryhope Pit.</i> Dark Grey, Softish, with Scales of Palaeonisc. Lowest Division.	<i>Ryhope Pit.</i> Yellow Laminated. Top Beds.	<i>Cullercoats.</i> Dark Grey, Hard Laminated
CaCO <sub>3</sub> ... ..	16·64	48·40	25·26
MgCO <sub>3</sub> ... ..	12·56	39·58	13·31
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> ... ..	3·76	3·26	7·6
Silica sol : in dilute acid ...	2·00	·26	—
Sand, etc. ... ..	45·12	7·8	29·53
Water, etc. ... ..	19·92	1·05	25·

At its base silica and alumina are its chief contents, but near the top carbonates of lime and magnesia form 80 per cent. of it; it may thus be looked upon as being a passage bed from the arenaceous bed beneath it to the calcareous above. It is never more than a few (3 to 5) feet thick, and, for such a thin deposit, is a remarkably persistent layer.

#### VIII.—LOWER LIMESTONE.

Within the area this Limestone reaches a maximum thickness of about 250 feet. In the northern part of the area its upper beds have been considerably disturbed, displaced, and in some cases entirely removed by thrusting (Fig. 3), so that it is difficult to be certain of its original thickness, but there is no doubt that it thickened rapidly from north to south, being some 20 feet at Marden, Whitley, 30 feet in Frenchman's Bay, and 250 feet beneath Humbledon Hill. It also appears to thin to the south of the area dealt with. There are excellent exposures of it in the quarries at Houghton-le-Spring and Hetton Downs.

It is always distinctly and regularly bedded, and where best developed its lower beds are of medium thickness (a few inches), its middle thinly bedded, and its upper coarsely (a foot or more). Its middle beds are often cellular and have incipient concretionary structures developed in them. It is often full of geodes, and hence has sometimes been called the "Geodic" Limestone. Its junction with the breccias above can be seen in many places as in Frenchman's

Bay, and with the Fossiliferous Limestone as at Down Hill Quarry, Claxheugh, Humbledon Hill, and in Tunstall Hope. Its top beds seem also to be exposed at Chourndon Point to the south of Seaham. It is of a yellowish or yellowish brown colour weathering to dark brown, and is often spotted with manganese dioxide and sometimes covered with arborescent crystals of this mineral. It is locally banded in various yellowish and brownish colours. Beds of marl are not interbedded with it in the area under discussion.

According to analyses by Kirkby and Browell the percentage of calcium carbonate in this limestone varies from 94.88 to 39.6; that of magnesium carbonate from 46.45 to 2.48. There appears to be a fairly large distribution of rock with about 90 per cent. of calcium carbonate.<sup>2</sup>

#### IX.—MIDDLE LIMESTONES.

The Middle division includes all the beds between the Lower bedded Limestones and the Flexible Limestone (or base of the Concretionary Limestones). It includes both bedded and unbedded rocks, but undoubtedly its most striking feature is the great mass of highly fossiliferous unbedded rocks reaching a maximum thickness of about 300 feet (see Section, Fig. 6). This latter division forms a distinct ridge of low rounded hills (referred to on page 245). Its western bounds have in the northern part of the area undergone denudation, but in the south it passes westwards into bedded rocks containing a very limited fauna. These beds can be seen near Silksworth and Murton and are well developed in Haswell Quarry. On the east it thins out, being replaced by bedded rocks, unfossiliferous and often highly brecciated. There are thus three distinct facies of this Middle division. It is difficult to decide whether the rocks on the east were deposited on the flanks of the unbedded ridge, or were laid down synchronously with it. The sec-

<sup>2</sup> *Op. jam. cit.*, pp. 213-220.

tion in the railway cutting near Ryhope Colliery shows a breccia of the Middle bedded division resting on a bed of marl and sand with the Fossiliferous limestone underneath, while the section to the north of Hawthorn Dene apparently shows the unbedded deposit passing gradually into the other division.

The bedded yellow rocks of the Middle division pass directly up into the Upper Limestone, but the relation of the Fossiliferous division to the Upper is undecipherable within the area, as the actual top is everywhere denuded. A section at Easington (to the south of the district) and general considerations from the contour of the region would make it appear that the Middle unbedded fossiliferous ridge may have been in the south the stratigraphical equivalent of part of the Upper Limestone, as well as the bedded division of the Middle. Howse<sup>3</sup> and Kirkby<sup>4</sup> both recognised this equivalence, although they did not quite appreciate its significance.

As a rule this division is highly magnesian (magnesium carbonate up to 40 and 50 per cent.), but in some parts it contains a very high percentage of calcium carbonate (98-99 per cent.). The latter rock has been produced from the former in some cases by the leaching out of the magnesium carbonate and segregating of the calcium carbonate (see page 306). It is seldom concretionary, but locally along fissures it has been rendered crystalline, more calcareous and concretionary. This can be best seen along a fissure on the south hill at Tunstall.

Some of the limestones in this division are foetid.

<sup>3</sup> Howse. See ideal section across the Magnesian Limestone terrace. Notes on Permian System of Durham and Northumberland. *Annals and Mag. of Nat. Hist.*, Jan., 1857, p. 6.

<sup>4</sup> Kirkby writes, "sometimes the limestone under its fossiliferous form is seen resting on the lower beds or compact limestone as at Humbledon Hill and Claxheugh, and sometimes the limestone under its cellular or pseudo-brecciated form is seen in exactly the same position as at Trow Rocks, Down Hill, Ryhope Pit and Fulwell Water Works." Note on "Geology of Baker and Tate's New Flora of Northumberland and Durham," *Nat. Hist. Trans.*, vol. iii., Part 2 (1870) p. 357.

(a) *The Fossiliferous Middle Limestone.*

This is a very variable division. It is sometimes a soft yellow highly magnesian fossiliferous limestone; at other places it is a hard, whitish, more calcareous fossiliferous rock. Some of the fossiliferous parts are brown, due to impregnation with iron,<sup>5</sup> and it is also locally (Tunstall Hills) very dark because it contains manganese dioxide. At other places it is a hard crystalline non-fossiliferous highly calcareous rock, parts of which, if not all, have been altered from the soft yellow fossiliferous limestone by the leaching out of the magnesian carbonate, this dedolomitisation being accompanied by the production of a cellular structure and a complete obliteration of the fossils (see solution-cavities, page 306, and photograph, Fig. 17).<sup>6</sup> It is sometimes highly brecciated, and from many parts of this breccia the fossils have been obliterated. From a piece of the breccia on Tynemouth Cliff King obtained 21 species,<sup>7</sup> and from the breccia at Blackhall Rocks C. T. Trechmann has collected several specimens. In Ford quarry, near Claxheugh, fossils—more or less indistinct—have been obtained from the breccia. The breccias are more calcareous than the fossiliferous rock from which they were originally derived. The obliteration of the fossils from the breccia and other changes makes it difficult

<sup>5</sup> A brown limestone locally developed in Fox Cover Quarry contains 5% of ferric oxide.

<sup>6</sup> Analysis of limestones from this division\* :—

	Yellow Highly Fossiliferous Limestone, Fox Cover Quarry, Seaham Harbour.	White Crystalline Limestone, derived from first, fossils obliterated, same locality.
CaCO <sub>3</sub> ... ..	58.02	98.84
MgCO <sub>3</sub> ... ..	38.33	.74
SiO <sub>2</sub> ... ..	.35	1.
Al <sub>2</sub> O <sub>3</sub> ... ..	.12	.12
Fe <sub>2</sub> O <sub>3</sub> ... ..	.13	.18

\* These changes can sometimes be seen in hand specimens (see page 306).

<sup>7</sup> Howse regarded this as being a brecciated piece of the Lower Limestone.

to decide to which of the two Middle divisions some of the breccias originally belonged. As a rule, this division is quite unbedded, and even when bedded, it is seldom very distinctly so. A variety south of Hawthorn Dene is distinctly oolitic, and contains arenaceous foraminifera cemented by crystalline carbonate of lime. As already stated this mass of unbedded (as a rule) fossiliferous limestone forms a distinct ridge running across country, thickening along its length as it is traced southwards, and thinning out laterally eastwards. It is generally denuded on the west, and its original top is also never seen, but it reaches a thickness of 180 feet at Tunstall Hill and about 300 feet further south. This limestone appears to have originally formed a shell bank in the Middle Permian sea, and many of the shells appear to have been drifted. It was deposited in a portion of the Permian sea that was fresher than the surrounding waters, and was thus able to support life in greater abundance. About 90 species occur in it, but it is exceedingly rich in individuals. It is the fossiliferous division of the Permian *par excellence*.

(b) *The Bedded Yellow Middle Limestones.*

The bedded yellow Middle Limestones lie on the eastern flank of the ridge of unbedded fossiliferous rocks. They form in general low ground, but are themselves entirely unfossiliferous. On the east of Tunstall Hill a bed of micaceous sandy marl occurs between the Fossiliferous Limestone and a brecciated bed belonging to this series. These beds were thus deposited on the flanks of a Middle Permian shell bank, although an exposure to the north of Hawthorn Dene would appear to prove that the two Middle divisions pass gradually into one another.<sup>8</sup> This is the

<sup>8</sup> Kirkby thought that there was no section showing the Cellular Limestone resting on the Fossiliferous or Shell Limestone, though there were many showing one passing from the Shell into one that is Pseudo-Brecciated on the same horizon, *op. jam. cit.*, p. 260.

principal brecciated zone, and corresponds roughly to the Brecciated and Pseudo-Brecciated Limestone of King and the Cellular of Sedgwick and Howse. They are exposed as bedded yellow rocks in the north end of Marsden Bay beneath the Flexible Limestone; they occur as highly brecciated beds along the banks of the Wear to the west of Sunderland Bridge, here also beneath the Flexible Limestone; in the same position they form the cliff along the coast from the thrust plane at the Craggs, Hendon, southwards to Seaham Harbour; and are continued south of this place nearly to Hawthorn Dene (Fig. 9). The percentage of magnesia is generally high in these beds.<sup>9</sup>

Both in Marsden Bay and along the coast south of Sunderland, beds belonging to this division have been silicified, bands and nodules of chert being of frequent occurrence.<sup>10</sup>

## X.—THE UPPER LIMESTONES.

### (a) *The Flexible Limestone.*

The Flexible Limestone is a thinly bedded yellow limestone of about 12 feet in thickness, whose laminæ possess the property of flexibility.<sup>11</sup> Most specimens lose this property on drying, but others certainly do not. G. W. Card, A.R.S.M., has shown that the flexibility depends on the abundance of minute empty spaces arranged promiscuously through it and parallel to the bedding, and also that the structure revealed in a thin section by high magnifying powers suggests the possibility that many of the grains are interlocked in such a way as to permit of a certain amount of movement on one another.<sup>12</sup> It contains a high percent-

<sup>9</sup> An analysis of it from Hendon gives 37·79 per cent. of Magnesium Carbonate, and another from Seaham Harbour 39·2 per cent.

<sup>10</sup> Chert is also recorded from these beds by R. C. Clapham from Fulwell railway cutting, SiO<sub>2</sub> 96·5 per cent., *Fyneside N.F.C. Trans*, vol. v., p. 24.

<sup>11</sup> Some laminæ of the bedded Middle are also slightly flexible, but such layers are quite locally developed.

<sup>12</sup> "On the Flexibility of Rocks with special reference to the Flexible Limestone of Durham," *Geol. Mag.*, Sec. III., vol. ix. (March, 1892), No. 233, p. 117.







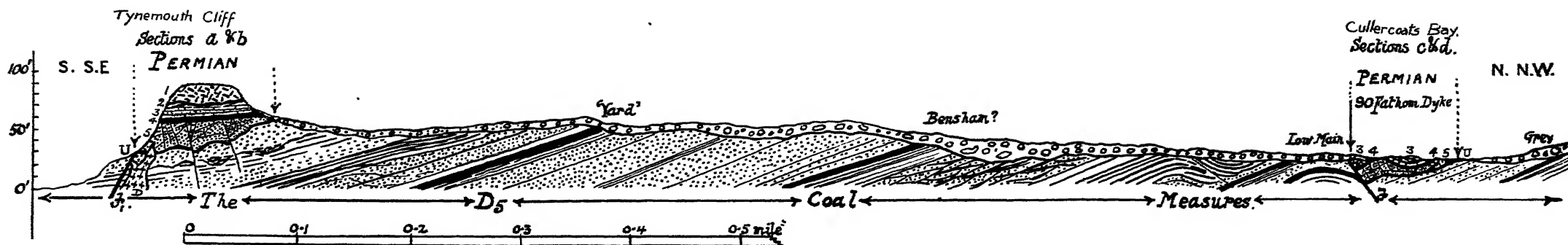


FIG. 8.—SECTION FROM TYNEMOUTH TO CULLERCOATS BAY, SHOWING THE TWO PRINCIPAL PERMIAN OUTLIERS IN NORTHUMBERLAND.—S. R. Haselhurst.

1. Brecciated Middle Limestone.
2. Thrust plane with disturbed beds beneath.
3. Lower Limestone (with arenaceous limestone on Tynemouth cliff).

4. Marl Slate.
5. Yellow Sands.
- U. Unconformity.
- F. Ninety Fathom "Dyke."

Sections a, b, c, d, are given on page 310.

F<sub>1</sub>. Fault south of Tynemouth.

D. Tynemouth Basaltic dyke.

The exposure is covered with boulder clay more or less along its whole length.

10° E of S

### General Section of the Coast

10° W of N

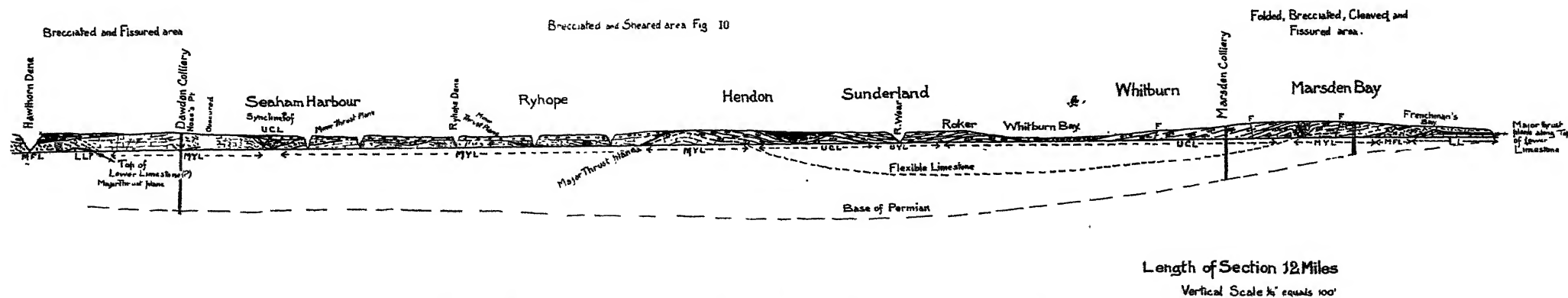


FIG. 9.—GENERAL SECTION OF THE COAST, SHOWING LIE OF THE BEDS AND POSITION OF THE CHIEF THRUST PLANES.—D. Woolcott.

- L.L. Lower Limestone.  
M.F.L. The Middle Unbedded Fossiliferous division, highly brecciated in both exposures shown.  
M.Y.L. Middle Yellow Bedded Limestone.  
U.C.L. Upper Concretionary Limestone.  
U.Y.L. Upper Yellow Limestone of Roker.

The major thrust plane at north end of section along top of Lower Limestone, seems to underlie nearly the whole district.  
The Middle Limestone is thrust over the Upper between Ryhope and Hendon. (See Fig. 10.)  
Some faults (F.) are shown.

The boulder clay and other superficial deposits are indicated by shading where they are thick.

The section in Frenchman's Bay and Marsden Bay is fully described in a paper on this area in the University of Durham Philosophical Society's Memoir No. 1.



age of magnesia as a rule. In the above-named paper an analysis of it made under the superintendence of G. W. Tate, A.R.C.S., is given as follows:—

CO <sub>2</sub>	...	...	...	46·476
CaO	...	...	...	30·744
MgO	...	...	...	21·169
FeO	...	...	.	·518
SiO <sub>2</sub>	...	...	...	1·028
			.	99·935

It is a remarkably persistent bed in the northern area, but I have not yet been able to trace it in the southern. It occurs at Marsden, and again on the coast at Hendon, south of Sunderland (see Sections, Figs. 9, 10). I have also noted it beneath Bildon Hill (Fig. 6) and below Sunderland Bridge. At Marsden fish remains have been found in it, and a finely laminated bed with the same genera in it, that occurs at the base of the Upper Limestone in Fulwell Quarries, is on the same stratigraphical horizon, and probably represents the Flexible Limestone under a slightly different aspect.<sup>3</sup> At Hendon beneath the thrust plane (Fig. 10) it becomes calcareous, crystalline and concretionary by the leaching out of the magnesium carbonate from it. Palæontologically it is important as it is the first bed above the Marl Slate and lower beds of the Lower Limestone in which fish remains have been found, and in the Marsden area invertebrata soon come in above it, although there are none in the bedded yellow rocks beneath it.

Lithologically it is of distinct interest as above it everywhere the rocks soon begin to assume the true concretionary aspect. It thus serves as a well-marked line of division between the bedded yellow Middle Limestones and the varied series of the Upper division. It also marks a distinct change in conditions. It is in some respects very like the

<sup>3</sup> See Kirkby, "On some Remains of Fish and Plants from the Upper Limestone," *Quart. Jour. Geol. Soc.*, vol. xx. (1864), pp. 345-358.

purser beds of the Marl Slate, and the occurrence in it of fish remains as in that deposit, makes it appear probable that it was deposited under similar tranquil conditions. It seems to mark a decrease in the depth of the Permian Sea, indeed the area over which it and the Concretionary Limestone were deposited was much more restricted than that over which the Lower and Middle Limestones were laid down.

(b) *The Concretionary Limestone.*

The Upper beds above the Flexible Limestone are divisible into two divisions, the lower of which is characterised by an unique development of concretionary structures. It is a bedded deposit varying from thinly laminated beds to thick deposits of embedded "marl."<sup>4</sup> This series lies in the form of a syncline beneath Sunderland (Section, Fig. 9) and forms the hills of Cleadon, Fulwell and Bildon. In the northern part of the area—Cleadon Hills and Marsden—it reaches a maximum thickness of some 300 feet, thinning, however, very much to the south.

This division consists of several interbedded deposits, which are known to the quarrymen under distinct names. The most characteristic deposits are the cellular and globular Concretionary Limestones—the "greystones" of the Marsden and Fulwell quarrymen, and the "Honeycomb or Main Limestone" of Fulwell are of this character. Associated with these are bedded non-concretionary (or incipient concretionary) limestones, (compact, brown, light and dark grey, sometimes bluish) which comprise the "bluestones" of Marsden and the "whitestone" of Fulwell. There are also beds of so-called "marl" or soft powdery yellow limestone. The Great Marl Bed at Fulwell is 40 feet thick. Some of these persist for considerable distances, but many are quite local, thinning out or passing gradually into brown non-

<sup>4</sup> Many of the so-called marls in the Permian do not contain more aluminous impurities than parts of the limestone. The term marl is thus somewhat misleading. (See analysis of Great Marl Bed on the next page.) They are always highly magnesian, soft and powdery.

concretionary limestones. At the base of the Concretionary Limestone at Marsden there is a development (over 100 feet) of brown limestone with thick, irregular interbedded masses of hard, grey limestone, which do not occur to the south in the Sunderland area.

ANALYSES<sup>5</sup> OF SOME TYPES OF THE CONCRETIONARY LIMESTONE.

	Bluestone from Byer's Quarry, Marsden.	Cellular greystone from main or honeycomb limestone, Fulwell Quarries.	Botryoidal limestone, Fulwell Quarries. Analysis of small grape-like concretions only (marly coating neglected).	Highly crystalline beds with numerous ennomotrace, and broken specimens of <i>Asymmetria</i> , Byer's Quarry, Marsden.	Marl from Great Marl Bed, Fulwell Quarries.		Grey spherical concretions embedded in soft yellow marl, Fulwell Quarries.	
					Bottom.	Top.	Concretions.	Marl.
CaCO <sub>3</sub> ...	97·84*	96·55	91·95	96·94	55·48	52·10	95·58	56·53
MgCO <sub>3</sub> ...	1·3	1·46	2·06	1·66	40·92	44·04	2·36	38·54
SiO <sub>2</sub> ...	·5	1·06	5·26	·6	3·04	2·73	1·4	3·6
Fe <sub>2</sub> O <sub>3</sub> & Al <sub>2</sub> O <sub>3</sub> ...	·26							
Water, etc. ...	·2	·93	·73	·8	·56	1·13	·66	1·33

\* Some analyses of this rock give a higher percentage of calcium carbonate than this.

The least magnesian of these beds are the compact bluestones, and the most magnesian are the marls, the greystones being intermediate. The greystones are largely cellular Concretionary Limestone (see page 305). The beds with the largest percentage of magnesia are not the most cellular, as might be expected if dolomitisation had taken place subsequent to deposition. The marls besides being the most magnesian generally contain the largest amount of siliceous and aluminous impurities. The amount of magnesia originally present in the beds before the concretionary structures began to be developed, would certainly, as Garwood has already pointed out,<sup>6</sup> seem to have been the

<sup>5</sup> Most of these analyses are from the paper by Kirkby and Browell.

<sup>6</sup> Garwood, *Geol. Mag.*, New Series, vol. viii. (Oct. 1891), pp. 433-440. B.A. Abstracts, Bradford, 1900, Section C.

determining factor in the setting up of these structures, and the presence of siliceous and argillaceous impurities appears to have had a deterrent effect. It is certain that the compact beds composed almost entirely of calcium carbonate (bluestones, etc.), have not had, or sometimes have only slightly had, a concretionary structure developed in them, and similarly neither have the very impure and highly magnesian marls, but the greystones (beds now intermediate in character, and in spite of much leaching out of magnesium carbonate, almost certainly of an intermediate type before the concretionary structures began to form) have had a complicated series of concretionary forms developed in them. Dr. Abbott has classified these structures and has shown that there appears to be a gradual development of some particular types.<sup>7</sup> He has also made a unique collection of photographs of them. Jukes-Browne suggested that the calcium carbonate was deposited in concretionary form,<sup>8</sup> and Green that the rock was originally a tufaceous deposit, the concretions being in part due to irregular precipitation, and in part to later rearrangement,<sup>9</sup> but there can be no doubt that, as Sedgwick pointed out in 1835,<sup>10</sup> they were developed in the rock after deposition, as the bedding planes had been formed in the rock before the concretionary action began. In 1889 Howse proposed that the "conglobated" type (spherical concretions) were stalactitic in origin,<sup>11</sup> but Garwood brought forward evidence to show that they were really segregations of calcium carbonate from the beds in which they occur.<sup>12</sup> It is noteworthy that where a spherical concretion is embedded in a matrix, the cement is always

<sup>7</sup> Abbott, *Trans. of Geol. Assoc.*, vol. xviii. (1904), pp. 322-324. *Proc. of Geol. Soc.*, vol. lxii., Pt. 3, No. 247, p. cxxxv. Concretions in *S. E. Naturalist*, 1907.

<sup>8</sup> Jukes-Browne, *Geol. Mag.* (Nov. 1891), p. 528.

<sup>9</sup> Green, B.A. Report, Newcastle (1889), p. 597.

<sup>10</sup> *Op. jam. cit.*, p. 87, *et seq.*

<sup>11</sup> *Tyneside Nat. Field Club*, Oct. 1889.

<sup>12</sup> *Op. jam. cit.*, pp. 425-426.

more highly magnesian than the concretion. It seems certain that we shall never completely understand them, nor many other difficulties connected with the magnesian limestone, until more is known regarding the solubilities of calcium and magnesium carbonates in presence of one another and of other substances, and until more experiments have been made on the growth of concretionary structures.<sup>3</sup> It appears important to note that apparently by the leaching out of the magnesium carbonate from other divisions of the limestone (Flexible Limestone at Hendon, Fossiliferous on Tunstall Hills<sup>4</sup>) they have been rendered crystalline and concretionary, and it seems probable that an explanation of most—if not all—of the concretionary action is the segregating of the calcium carbonate as the magnesium carbonate is being leached out. While undoubtedly the main concretionary structures were developed in the Permian by segregation long ago<sup>5</sup> (probably shortly after deposition, and certainly before the thrusting and folding to which the rocks have been subjected), yet I see no reason why under special conditions, as where a leaching out of the magnesium carbonate is taking place along fissures, etc., concretionary action may not be sometimes proceeding now.

These structures may for field purposes be divided into spherical and cellular. In the development of the spherical—the cannon-ball, botryoidal and stellate—fossils have occasionally acted as nuclei, but this is by no means always

<sup>3</sup> See Rainey's experiments in Carpenter, "The Microscope and its Revelations," 7th edit. (1891), p. 1021; and Stocks, "On the Origin of certain Concretions in the Lower Coal Measures," *Quart. Jour. Geol. Soc.*, vol. lviii. (Feb. 1902), pp. 46-58.

<sup>4</sup> On the coast just north of Byer's Quarry, Marsden, an irregular brecciated mass seems to have had a crystalline concretionary structure impressed on it subsequent to brecciation.

<sup>5</sup> Kirkby writes: "There does not seem to be much doubt that the difference in chemical composition is largely due to segregation after deposition." He regards the concretions as having been produced in this way, and also some of the alternations of crystalline and earthy strata and laminæ as being due to the same cause, not to difference in the sediment deposited, *op. jam. cit.*, p. 228.

the case. Indeed in the concretions at Fulwell I have never found any fossils, although they are fairly common in the Marsden area. The cannon-ball type is sometimes hollow at the centre (the hole seldom appearing to be the cast of anything), but sometimes they are solid throughout; occasionally they have a concentric structure, more often a radial, but they are sometimes structureless. The radial structure seems generally to start from the outside and grow inwards. They are often enveloped in a yellow, highly-magnesian matrix, although there is sometimes little cementing material. Fossils have played little or no part as nuclei in the development of the cellular, honeycomb and other types. It seems certain that the bedding planes were formed before the concretionary structures were set up as they often act as dividing lines, but it is exceedingly difficult to understand the cause of the other lines anastomosing through the rock, which have apparently acted as guiding lines for the concretionary growths.

(c) *The Upper Yellow Limestone.*

Lying on the Concretionary Limestone is about 100 feet of yellow bedded limestone which is confined in the north of Durham to the Sunderland district (see Sections, Figs. 6, 7 and 9). It is best exposed at Roker and on the foreshore in front of Sunderland Docks. It also outcrops in the Hartlepool district. It is sometimes compact and crystalline, but is often pseudo-oolitic in appearance, being composed of minute hollow spheres. This structure is a concretionary one. Ripple marks were observed in this limestone by King.<sup>6</sup> It is occasionally fossiliferous. An analysis of a vesicular-looking variety at Roker is given by Browell and Kirkby as follows<sup>7</sup>:— $\text{CaCO}_3$ , 59·81,  $\text{MgCO}_3$ , 26·06,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , 0·53; water, etc., 13·6.

<sup>6</sup> *Op. jam. cit.*, p. xiv

<sup>7</sup> *Op. jam. cit.*, p. 227.



## XI.—THE PALEONTOLOGY OF THE PERMIAN OF THE AREA.<sup>8</sup>

(In collaboration with C. T. Trechmann, B.Sc.)

The palæontology of the Permian of Durham and Northumberland presents marked peculiarities in regard to the distribution of the fossils; the paucity of the number of genera and species (especially in the upper divisions); and the small size to which the individuals attain. There can be little doubt that the conditions under which the creatures lived was detrimental to their development, the Permian thus being in this area a period of decadence. Such conditions would be produced in an isolated sea undergoing dessication. As this sea in which concentration was taking place would contain a large proportion of the salts which were eventually deposited during the period, it does not affect this argument to any great extent whether the more fossiliferous parts of the limestone were highly magnesian originally, or whether the magnesia was introduced subsequent to deposition.<sup>9</sup> That the sea may have been purer during certain times and at certain parts seems evident, and during such periods or in such places life would be more prolific.

The total number of species found in the area is about 120, and their distribution is associated with the lithological divisions already established. The Magnesian Limestone proper is divisible into two well-defined palæontological groups—the Lower and Middle Fossiliferous Limestones and the Upper series of beds. The former constitute one group because all the fossils found in the Lower Limestone—with the exception of two species—occur in the Middle division. The fauna of the Middle Fossiliferous Limestone is, however, in the variety of species and profusion of individuals in marked contrast with that of the Lower beds.

<sup>8</sup> Much of the subject-matter under this heading applies to the whole of the Permian of Northumberland and Durham.

<sup>9</sup> See page 249 *et seq.*

There was a sudden influx of genera and species at the beginning of the deposition of the Fossiliferous Limestone, and during the deposition of this bed life in one part of the Permian sea was very prolific. Of this fauna the Brachiopoda and Polyzoa were the most thriving communities, but they die out soonest. Undoubtedly the most marked feature of Permian palæontology is that no brachiopods, no polyzoa, no corals, no echinoids, and no cephalopods have ever been found above the Fossiliferous division of the Middle series; only a few species of fish, lamellibranchs, gastropods, entomostraca, foraminifera and plants are known to occur in the rocks above the Flexible Limestone. That the conditions were different under which the two major divisions were deposited is evident from the contrast in their fauna and the markedly distinct lithological peculiarities. The main change was probably a lessening in the depth and extent of the sea within the area. King, Howse and Kirkby collected in the Permian so thoroughly,<sup>10</sup> that no new species—except some arenaceous foraminifera—have ever been found by collectors since. This appears to indicate that the fauna was a very restricted one, and that little variation was taking place in the individual species. Owing to the conditions the fauna was not a progressive, but a decadent one.

The invertebrate fossils in the Permian are largely found as casts, but in certain localities good specimens with well preserved shells occur. Sometimes the shell is hollow, in which case the internal parts (as the "spire" of Brachiopods) are well preserved. More generally, however, the shell has been dissolved away, and an internal cast is preserved by an infilling of yellow Magnesian Limestone and an external one in the matrix. In a few cases the infilling is crystalline calcium carbonate. In a thin crystalline bed in the Concretionary Limestone at Byer's Quarry, Marsden, the shell substance has become crystalline also.

<sup>10</sup> See list of palæontological papers, page 235.

The characteristics of the divisions of the Permian are as follows :—

(a) The upper red beds with salt :

Howse and Dr. Veitch record *Myalina Hausmanni*, *Axinus dubius* and *Chondrites virgatus* from the limestone in the cores from borings made through these beds in the south of Durham.<sup>1</sup> None of these are restricted.

(b) The Upper Limestones :

The fauna of these beds is very poor in species, and (except on one or two horizons) the number of individuals is very few.

(1) The Upper Yellow Limestone.

The species found in these beds are *Axinus dubius*, *Pleurophorus costatus*, *Myalina Hausmanni*, *Turbo Permianus*, and *Chondrites virgatus*. None restricted.

(2) The Concretionary Limestone.

The fauna includes :—

Foraminifera, 5 species.

*Dentalina*.

*Textularia*.

*Trochammina*.

*Annulosa*.

*Spirorbis Permianus* (King).

Entromostraca.

*Cythere* (several species).

*Kirkbya Permiana* (Jones).

Gastropoda.

*Turbo Permianus* (King).

Lamellibranchiata.

*Gervillia antiqua* (Münst).

*Myalina Hausmanni* (Goldf).

*Leda speluncaria* (Gein).

*Pleurophorus costatus* (Brown).

*Axinus dubius* (Schl).

<sup>1</sup> Howse "Note on South Durham Salt Borings, etc.," *Nat. Hist. Trans. of Northd. and Durham*, vol. x. (1889-90), pp. 220-226 ; and Guide to collection of Local Fossils, Museum, Newcastle, 1889, p. 5.

This invertebrate fauna is found chiefly in the Marsden area in North Durham.<sup>2</sup> None of the lamellibranchs or gastropods are restricted, and all the other species have been obtained from one crystalline bed that occurs in Byer's Quarry, Marsden.

Besides these some fish and plant remains were obtained from (and are still occasionally found in) the lower beds of this division in Fulwell Quarries and from the Flexible Limestone at Marsden.

#### Pisces.

*Acentrophorus varians* (Kirkby).

*Acentrophorus Abbsii* (Kirkby).

*Acentrophorus altus* (Kirkby).

*Acrolepis Kirkbyi* (Howse).

#### Plantæ.

*Calamites Wakei* (Howse).

*Ulmannia selaginoides* (Sternb).

#### (c) The Middle Fossiliferous and Lower Bedded Limestones:

These form a distinct group marked by the presence of *Productus Horridus*.

All the invertebrata found in the Lower Limestone with three exceptions—*Astarte Valisneriana* (King), *Chonetes Davidsoni* (Schaur), and *Lingula Credneri* (Gein),<sup>3</sup> pass up into the Middle division. The number of species occurring in the Lower Limestone is only about half of those found in the Fossiliferous Limestone (about 90), and a very much more marked difference is found in the small number of individuals in the Lower as compared with their profusion in the Middle division.

##### 1. The Fossiliferous Limestone.

This division (as a rule unbedded) is very rich in individuals (hence the name often given to it "The Shell

<sup>2</sup> A similar Fauna occurs in a Concretionary Limestone, interstratified with a platy fossiliferous limestone to the south of Blackhall Rocks, So. Durham.

<sup>3</sup> The first two are restricted to the Lower Limestone, the last occurs in the Marl Slates as well.

Limestone"). Exposures of it are numerous along the ridge of Fossiliferous rock already noticed (page 245). Boldon Hills, Claxheugh and district, Humbledon Hill, Tunstall Hills, west of Ryhope, Dalton-le-Dale and Fox Cover Quarry, Seaham Harbour, are all good collecting grounds. Several species are restricted to this limestone. As already stated there was an influx of genera and species into the area, and a great increase in the number of individuals during the time this bed was being deposited. Towards the end of its deposition there was an equally marked decrease in the fauna. One of the peculiarities of this bed is the manner in which the species occur together, they are not arranged in bands, but are to a large extent scattered promiscuously through the rock. A large number of the specimens in this division are broken, and it would seem probable that some of them had been drifted into the place in which they occur. Certain localities are richer in particular groups than others—*e.g.*, gastropods (*Pleurotomaria antrina*, etc.), are most numerous in the limestone of Tunstall Hill.<sup>4</sup> The bryozoa are sometimes very numerous, and it is interesting to find that the bryozoa reefs that occur in the Zechstein of Thuringia belong to the same horizon as the Lower and Middle Limestones of Durham. Numerous specimens of entomostraca, a foraminifer, and minute brachiopoda, etc., occur in pockets of marl on Tunstall Hill, and an oolitic-looking variety from the coast south of Hawthorn Dene contains arenaceous foraminifera cemented by crystalline carbonate of lime.

Large areas of this limestone have been brecciated, and the fossils entirely or partly obliterated from the breccia, and obliteration of the fossils has also been brought about by the leaching out of the magnesian carbonate from the limestone, and its conversion into a crystalline, cellular highly calcareous rock.

<sup>4</sup> At Quarry Heads near Ryhope there is a bed almost entirely composed of small gastropods.

The fauna includes :—

\* Species marked with an asterisk are found in the Lower Limestone as well as in the Fossiliferous.

Algæ.

*Palæophycus insignis*\* (Gein).

*Chondrites virgatus* (Münst).

Foraminifera.

*Trochammina pusilla*\* (Gein).

Porifera.

*Eudea tuberculata* (King).

*Mammilliopora mammillaris* (King).

*Bothroconis planta* (King).

*Tragos Tunstallensis* (King).

Actinozoa.

*Polycælia profunda* (German).

*Calamopora Mackrothi* (Gein).

*Stenopora columnaris*\* (Schl).

Echinodermata.

*Archæocidaris Verneuiliana* (King).

*Cyathocrinus ramosus*\* (Schl).

Annulosa.

*Spirorbis planorbites* (Gein).

Entromostraca.

*Kirkbya Permiana* (Jones).

*Cythere* (several species).

*Prosopeponiscus paradoxus* (Schloth).

Bryozoa.

*Fenestella retiformis*\* (Schl).

*Synocladia virgulacea*\* (Gein).

*Thamniscus dubius* (Schl).

*Acanthocladia anceps*\* (Schl).

*Phyllopora Ehrenbergi*\* (Gein).

*Phyllopora multipora* (Shrubsole).

*Hippothoa Voigtiana* (King).

Brachiopoda.

*Discina Koninckii*\* (Gein) = *D. speluncaria* (Schl).

*Crania Kirkbyi* (Sow).

*Productus horridus*\* (Sow).

*Productus umbonillatus* (King) = *P. latirostratus* (Howse).

*Strophalosia Goldfussi*\* (Münst) and variants of Davidson).

*Strophalosia lamellosa*\* (Gein) and variants.

*Streptorhynchus pelargonatus*\* (Schl).

*Camarophoria multiplicata* (King) = *C. Humbletonensis* (Howse).

*Camarophoria Schlotheimi* (v. Buch) = *C. crumena* (Mart).

*Camarophoria globulina* (Phill).

*Spirifer alatus*\* (Schl) and variants.

*Spiriferina cristata*\* (Schl).

*Spiriferina multiplicata* (Sow).

*Martinia Clannyana*\* (King) = *Spirifer* (Dav).

*Athyris Pectinifera*\* (Sow) = *A. Roissii* (Léveillé).

*Terebratula elongata*\* (Schl) and variants.

*Terebratula sufflata* (Schl).

#### Lamellibranchiata.

*Pecten pusillus*\* (Schl).

*Pinna prisca* (Münst).

*Lima Permiana* (King).

*Monotis speluncaria*\* (Schl) and variants.

*Myalina Hausmanni* (Goldf) and variants =  
*Mytilus septifer* (King) = *Mytilus squamosus* (Sow).

*Gervillia antiqua*\* (Münst).

*Gervillia ceratophaga* (Schl) = *Bakwellia Sedgwickiana* (King).

*Gervillia Sedgwickiana* (King).

*Arca tumida* (Sow) = *A. striata* (Schl) and variants.

*Leda speluncaria*\* (Gein) = *L. Vinti* (King).

*Nucula Beyrichi* (v. Schauroth).

*Cardiomorpha modioliformis* (King) = *C. Pallasi* (de Vern).

*Allorisma elegans*\* (King) = *Myacites lunulata*  
(Keyserl).

*Pleurophorus costatus*\* (Brown).

*Solemya normalis*\* (Howse).

*Solemya biarmica*\* (de Vern).

*Schizodus obscurus*\* (Sow)  
and variants.

*Schizodus truncatus* (King). } = *Axinus dubius* (Schl)

*Edmondia Murchisonia* (King) = *E elongata*  
(Howse).

*Astarte Tunstallensis* (King).

*Tellina Dunelmensis* (Howse).

#### Gastropoda.

*Pleurotomaria antrina*\* (Schl).

*Pleurotomaria nodulosa* (King).

*Euomphalus Permianus* (King).

*Turbo helicinus*\* (Schl).

*Turbo Taylorianus* (King).

*Turbo Permianus* (King).

*Natica Liebnitziana* (King).

*Loxonema fasciata* (King).

*Loxonema Geinitziana* (King).

*Macrocheilus symmetricus* (King).

*Chiton* (various species, all of great variety).

*Dentalium Sorbyi* (King).

*Chemnitzia Roessleri*\* (Gein).

#### Pteropoda.

*Theca Kirkbyi* (Howse).

#### Cephalopoda.

*Nautilus (Pteriptoceras) Freieslebeni*\* (Gein) =

*Pteronautilus* (Meek).

Several species are restricted to this limestone, the commonest and most important of these being *Productus umbonilatus*, *Area tumida*, *Edmondia Murchisoniana*, and *Thamnis-  
cus dubius*.



The most common species occurring in this division are *Productus Horridus*, *Spirifer alatus*, *Camarophoria Schlotheimi*, *Strophalosia Goldfussi*, *Monotis speluncaria*, *Arca tumida*, *Terebratula elongata*, *Fenestella retiformis*.

From the Claxheugh area, which is at present one of the best collecting grounds, C. T. Trechmann has obtained the following fossils:—

1. In fragments of rock from landslip at Claxheugh. The horizon is the base of the Fossiliferous Limestone.

*Phyllopora* and other *polyzoa*.

*Spiriferina multiplicata*.

*S. cristata*.

*Monotis speluncaria*.

*Arca striata*.

*Gervillia ceratophaga*.

*G. antiqua*.

2. From old quarry (Claxheugh Quarry), south of Claxheugh. Horizon some 60 feet above the base of the Fossiliferous Limestone.

Actinozoa.

*Calamopora sp.*

Echinodermata.

*Cyathocrinus ramosus* (Schl).

(*Archæocidaris verneuiliana* also occurs D.W.)

Bryozoa.

*Fenestella retiformis* (Schl).

*Synocladia virgulacea* (Phil).

*Thamniscus dubius* (Schl).

*Acanthocladia anceps* (Schl).

Brachiopoda.

*Productus Horridus* (Sow).

*P. umbonillatus* (King).

*Strophalosia Goldfussi* (Münst).

*S. curvata* (Gein).

*S. Morrisiana* (King).

*Streptorhynchus pelargonatus* (Schl).  
*Camarophoria Schlottheimi* (v. Buch).  
*U. globulina* (Phil).  
*Spirifer alatus* (Schl) and variants *S. undulatus*  
 (Sow) and *S. cf. Permianus* (King).  
*Spiriferina cristata* (Schl).  
*S. multiplicata* (Sow).  
*Martinia cf. Clannyana* (King).  
*Terebratula elongata* (Schl).  
*T. cf. sufflata* (Schl).  
*Athyris pectinifera* (Sow).

#### Lamellibranchiata.

*Pecten pusillus* (Schl).  
*Lima Permiana* (King).  
*Monotis speluncaria* (Schl).  
*Monotis c.f. radialis* (Phil).  
*Bakevellia ceratophaga* (Schl).  
*B. Sedgwickiana* (King).  
*B. cf. bicarinata* (Schl).  
*Arca tumida* (Sow).  
*A. striata* (Schl).  
*Pleurophorus costatus* (Brown).  
*Schizodus cf. obscurus* (Sow).  
*Allorisma elegans* (King).

#### Gastropoda.

*Pleurotomaria nodulosa* (King).  
*P. antrina* (Schl).  
*P. sp., cf. Natica minima*.

He notes regarding this fauna (1) the profusion of individuals, (2) the scarcity of gastropods, (3) absence of Nautilus, Discina, etc., (4) the commonness of encrinital stems (in places it becomes an encrinital limestone), and (5) the general rarity or absence of Upper Limestone forms - absence of *Myalina*, and rarity of *Gervillia* and *Avinus*. It is a lower Fossiliferous Limestone fauna.

## 3. From quarry near Ford Hall (Ford Quarry).

*Camarophoria Schlotheimii* (v. Buch).*Terebratulula elongata* (Schl) and variants.*Strophalosia Goldfussi* (Münst).*Gervillia antiqua* (Münst).*G. ceratophaga* (Schl).*Mytilus squamosus*.*Pleurotomaria cf. antrina* and other gastropods.*(Discina Koninckii* also occurs D.W.)

This is probably a fauna (not yet obliterated) belonging to a brecciated part of the Fossiliferous Limestone, and from a higher horizon than the other two localities. (Fossils more or less distinguishable can be obtained from the breccia in this quarry. D.W.)

## 2. The Lower Limestone.

The species marked with an asterisk in the list of fossils from the Fossiliferous Limestone occur in the Lower Limestone also. The only species restricted to it are *Astarte Valisneriana* (King) and *Ghonetes Davidsoni* (Schaueroth). *Lingula Credneri* occurs in this Limestone and in the Marl Slate, but not in the divisions above. Howse and Kirkby state the commonest species are *Productus horridus*, *Spirifer alatus*, *Camarophoria Schlotheimi*, *Strophalosia lamellosa* and *Gervillia antiqua*. Few localities for collecting in this limestone are at present exposed, but specimens can be obtained in the disturbed beds at the west end of Claxheugh (in railway cutting), in Frenchman's Bay and one or two places along the escarpment.

In the lower beds of this division fish remains have been found. At Pallion *Platysomus striatus* (Ag), and at Down Hill, Boldon, *Palæoniscus comptus* (Ag). At Midderidge, south of the district discussed in this paper, an amphibian—*Lepidotosaurus Duffi* (Han. and Howse) has been found. These link the lowest Limestone beds with the Marl Slate beneath.

## (d) The Marl Slate.

The marked palæontological feature of this bed is the number and variety of the fish remains. These can be obtained at most of the exposures, and have been got from the sinkings through this bed.<sup>5</sup> That these remains are often contorted, though whole, was first pointed out by Hutton, and the inference that their death was caused by inroads of the salt waters of the inland sea into estuaries or coastal lagoons has been drawn by Professor Lebour.<sup>6</sup> At Mid-deridge the remains of a reptile has been found in it. Besides these some few marine invertebrata occur in this bed.

The fauna includes:—

## Annulosa.

*Microconchus? carbonarius* (Murch).

## Brachiopoda.

*Lingula Credneri* (Gein).

*Discina Koninckii* (Gein).

## Lamellibranchiata.

*Myalina Hausmanni* (Goldf.).

## Cephalopoda.

*Nautilus Freieslebeni* (Gein).

## Pisces.

*Palæoniscus comptus* (Ag.).

*Palæoniscus elegans* (Sedg.).

*Palæoniscus longissimus* (Ag.).

*Palæoniscus macrophthalmus* (Ag.).

*Acentrophorus glaphyrus* (Ag.).

*Pygopterus mandibularis* (Ag.).

*Acrolepis exculptus* (Germar).

*Acrolepis Sedgwickii* (Ag.).

*Platysomus striatus* (Ag.).

*Globulodus macrurus* (Ag.).

*Dorypterus Hoffmanni* (Germar).

*Coelacanthus granulatus* (Ag.).

<sup>5</sup> E. S. Wood, Dawden Sinking, *Trans. Inst. Min. Eng.*, vol. xxxii., 1906-7, p. 551.

<sup>6</sup> *Op. jam. cit.*, p. 331.

*Janassa bituminosa* (Schloth.).

*Woodnika striatula* (Münst).

Reptilia.

*Proterosaurus Speneri* (v. Meyer).

*Proterosaurus Huxleyi* Han. and Howse).

Plantæ.

Several species including *Ulmannia selaginoides*,  
*Chondrites virgatus*, *Calamites*, etc.

# LIST OF PAPERS DEALING WITH THE PALÆONTOLOGY OF THE AREA.

## SEDGWICK.—

Geol. relations and internal structure of the Mag. L. *Trans. Geol. Soc.*, second series, vol. iii. (1835).

## KING.—

Monograph on Permian Fossils. *Pal. Soc.*, 1850.

## HOWSE.—

1. Catalogue of the Fossils of the Permian System of Northumberland and Durham. *Newcastle*, 1848.
2. Notes on the Permian System of Durham. *Trans. Tyneside N. F. C.* (1858) and *Annals of Nat. Hist.*, 1857.
3. Catalogue of the Local Fossils in the Museum of Nat. Hist. Soc. *Nat. Hist. Trans. of North. and Durham*, vol. x. (1887-90) pp. 227-288, published as a Guide to the collections of Local Fossils in the Museum of Nat. Hist., Newcastle, 1889.
4. Note on the discovery in 1836-7 of a Fossil Fish (*Acrolepis Kirkbyi* n. sp) in the Upper Division of the Magnesian Limestone of Marsden. *Nat. Hist. Trans. of North. and Durham*, vol. xii., 1877-91, pp. 171-2.
5. Note on the South Durham Salt Borings with remarks on the fossils found in the Magnesian Limestone cores and the Geological position of the Salt. *Nat. Hist. Trans. of North. and Durham*, vol. x., 1887-90, pp. 220-226.

## HOWSE AND KIRKBY.—

A synopsis of the Geology of Durham and part of Northumberland. Pub. by *Tyneside N. Field Club*, Aug., 1863.

## KIRKBY.—

1. On some fossils from the Lower Limestone of Sunderland. *Trans. Tyneside N. F. C.*, vol. vi., pt. ii. (1864), pp. 212-220.
2. On the fossils of the Marl Slate and Lower Magnesian Limestone. *Nat. Hist. Trans. of North. and Durham*, vol. i., pt. ii. (1866), pp. 184-200.
3. On the Permian Chitonidæ. *Q. J. G. S.*, xv. (1859), pp. 607-626, and *Trans. Tyneside N. F. C.*, vol. iv., pt. iv. (1860), pp. 238-263.
4. On Permian entromostraca from the Shell Limestone of Durham. *Trans. Tyneside N. F. C.*, vol. iv., pt. ii., pp. 122-171 and *Annals and Mag. of Nat. Hist.*, third series, No. 11, Nov., 1858.
5. On some fish and plants from the Upper Limestone. *Q. J. G. S.*, vol. xx. (1864), pp. 345-358.
6. On the occurrence of *Lingula Credneri* in the Permian of Durham and the claim of these rocks to be entitled a system. *Q. J. G. S.*, vol. xvi. (Mar., 1860), pp. 412-421.
7. On the Permian Rocks of South Yorkshire and on their palæontological relations. *Q. J. G. S.*, vol. xvii. (March, 1861), pp. 287-325.
8. On some Permian Fossils from Durham. *Q. J. G. S.*, vol. xiii. (1857), pp. 213-218.

## DAVIDSON.—

The Permian Brachiopoda. *Pal. Soc.*, 1858.

## HANCOCK AND HOWSE.—

1. On *Janassa bituminosa* (Schlotheim), from the Marl Slate of Midderidge, Durham. *Nat. Hist. Soc. Trans. of North and Durham*, vol. iii. (1868-70), pp. 339-357.
2. On a new Labyrinthodont Amphibian from the Magnesian Limestone of Midderidge, Durham. *Nat. Hist. Trans. of North. and Durham*, vol. iv. (1871-2), pp. 219-221.
3. On *Proterosaurus Speneri* (von Meyer), and a new species *Proterosaurus Huxleyi* from the Marl Slate of Midderidge, Durham. *Nat. Hist. Trans. of North. and Durham*, vol. iv. (1871-2), pp. 232-242.
4. On *Dorypterus Hoffmanni* (Germar), from the Marl Slate of Midderidge, Durham. *Nat. Hist. Trans. of North. and Durham*, vol. iv. (1871-2), 243-268.

## HANCOCK AND ATHERY.—

On the generic affinity of *Climaxodus* and *Janassa*, two fossil fishes related to the Rays. *Nat. Hist. Soc. Trans. North. and Durham*, vol. iii. (1868-70), pp. 330-339.

## PALÆONTOLOGICAL HORIZONS OF THE PERMIAN.

Divisions.	Fig. 2.	Fish and Plants.	Zonea.	Commonest Species.	
Red beds with Salt.				Myalina Hausmanni. Axinus dubius have been found.	Fossils in these beds are not numerous, but invertebrata are fairly common in the Concretionary Limestone of Marsden area and fish in Fulwell Quarries. No brachiopods, bryozoa, cephalopods, corals, encrinurites have even been found in the beds above the Fossiliferous Limestone.
Upper Yellow.			No restricted species.	Myalina Hausmanni. Pleurophorus costatus. Axinus dubius.	
Concretionary Limestone.		(Acentrophorus, Acrolepis, Ulmannia, etc. (Fulwell Quarry).		Myalina Hausmanni. Pleurophorus costatus. Axinus dubius. Turbo Permianus.	Entomostraca, Foraminifera, Byer's Quarry, Marsden.
Flexible Limestone.		(Acentrophorus and Acrolepis (Marsden).	Local zone of Productus umbonillatus (King).	Productus horridus. Skophalosia Goldfussi. Spirifer alatus. Terebratulula elongata. Fenestella retiformis.	Very rich in individuals. About 120 species. Brachiopods and bryozoa specially numerous. Several species are restricted.
Middle Limestones — a Fossiliferous Limestone. b Bedded Yellow.			Local zone of Chonetes of Davidsoni (Schauinsland).	Productus horridus. Spirifer alatus. Fenestella retiformis.	Fossils similar to Fossiliferous Limestone, but only about 30 species. Only two or three restricted species. Individuals scarce. A few species of marine invertebrata in Marl Slate.
Lower Limestone.		Platysomus, Lepidotosaurus, Proterosaurus, Palaeoniscus, Ulmannia, etc.			
Marl Slate.				No fossils.	
Yellow Sands.					

## XII.—THE THRUSTING.

The Permian rocks of this area have been subjected to horizontal pressures, which have produced: a decrease in the lateral extension of the Magnesian Limestone, numerous horizontal, oblique and vertical fractures, lateral displacement, folding, a general shattering of parts of the strata and many structures such as have been proved to have been developed by thrust movements in other areas. They have brought about internal Permian ructions of a pronounced character. The most interesting district is undoubtedly Marsden,<sup>7</sup> since movements appear to have taken place towards this area from two opposite directions, the effect of a "Horst" being so produced, and thus the phenomena are here more complicated than at any other place. Outside this zone the evidences of movement obtained are all probably in one definite direction at the particular point of observation which direction may be inclined at a considerable angle to that of the main thrust. That the pressures were horizontal or nearly so is proved by the vertical cleavage at Marsden, the vertical slickensided planes and cleavages at Jane Jiveson's rock (Fig. 10) and the horizontal nature or general low hade of the thrust planes.

It is perhaps noteworthy that no torsional movement on a large scale can be proved. The cleavage at Marsden is twisted at one point, but this feature would appear to be quite local.

Since the beds of the district vary in rigidity, flexibility, compressive strength, brittleness, etc., the thrusting has necessarily had quite varied effects on them. As already indicated the accentuation of the Coal Measure syncline beneath Sunderland is probably a result of the thrusting, as the secondary folding of the coal basin coincides with that of the Permian above it. The evidences of lateral movement that are found in the Coal Measures at the base of Tynemouth Cliff, in the cliff south of the Ninety Fathom

<sup>7</sup> Woolacott, *Univ. of Durham Phil. Soc. Mem. No. 1* (1909).







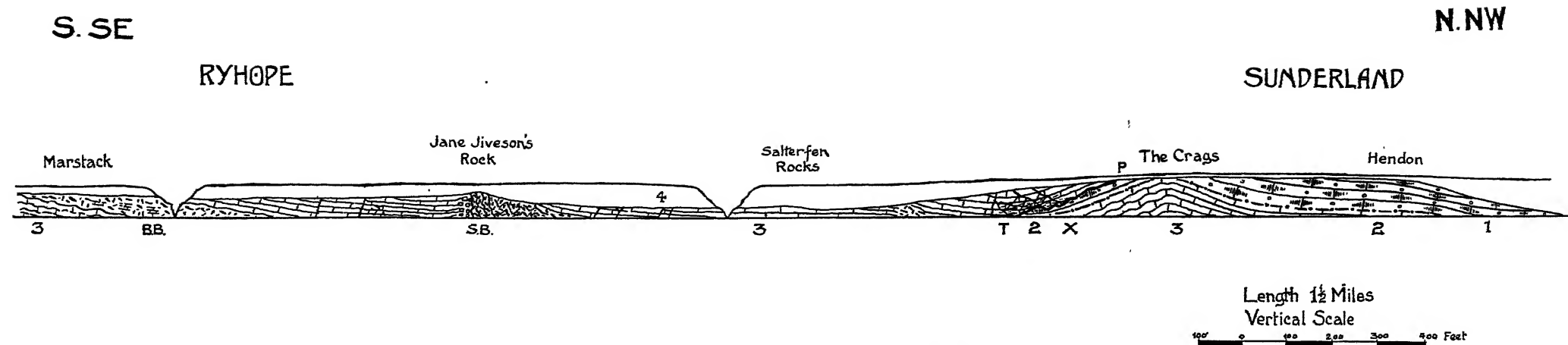


FIG. 10.—SECTION ALONG THE COAST SOUTH OF SUNDERLAND, FROM HENDON TO RYHOPE.

1. Upper Concretionary Limestone.
2. Flexible Limestone.
3. Upper Middle Bedded Limestone.
4. Superficial deposits.
- T.P. Thrust plane.
- S.B. Intruded, slickensided and cleaved breccias.
- B.B. Brecciated Bed.

Description of section: At Hendon the Upper Concretionary Limestones rise from beneath the boulder clay. They are typical cellular concretionary rocks. The beds lie in the form of an anticlinal, and beneath them is the Flexible—here well developed—and the Upper Middle Limestones. In the latter rock there are some bands and nodules of chert, many irregular geodes with calcium carbonate infilling and

many cavities. The soft yellow bedded Middle Limestone are minutely folded. At X. there is some brecciation and the Flexible Limestone becomes harder, more crystalline and less magnesian. Along the thrust plane the Middle Limestones have been thrust over the Flexible and lower Upper beds. The hade of the fault is to the south. The throw possibly 60' + and the displacement 250'(?). Above the thrust plane the Middle beds are intensely fractured into large blocks—"block fractured"—the fissures being generally cemented, and strain-slip and phacoidal structure has been developed in them by shearing (see photograph, Fig. 14).

From here to the Marstack all the beds belong to the bedded Middle Permian. At Jean Jiveson's rock which projects about 100 feet from the cliff face, there is a cleaved mass of breccia cut by vertical slightly curved slickensided planes. The breccia on its northern side is folded, and on its

southern side broken masses of the yellow limestone lie against it. It appears to have been forced up from the beds beneath—"intruded breccia"—and it is possibly connected with the thrust plane to the north. It may be looked upon as a highly brecciated, fractured and faulted anticlinal.

Along the coast between this rock and the Marstack (1" maps) there are several fractures in cliff, and several small forced up masses of breccia occur on the foreshore. At the Marstack a brecciated bed with a slickensided plane occurs. It rests on a very disturbed base (a minor thrust plane) and the beds beneath are much fractured.

The whole of the beds are overlaid by a variable thickness of superficial deposits (4) which are left unshaded.

The vertical scale is rather more than twice the horizontal.



"Dyke" at Cullercoats,<sup>8</sup> and at Whitley<sup>9</sup> would appear to have been produced synchronously with the movements in the Permian rocks above. In the Coal Measures the thrusting is marked by a movement of the more rigid sandstones along shales or sandy shales and along a line of local unconformity at Whitley.<sup>9</sup>

The thrusting has thrown the whole of the Permian series into broad folds (Fig. 9), and has produced (see effects of the thrusting page 295) markedly different results on the several beds of the series.

In the small amount of local folding in the principal brecciated zone, the damping down of the folds at Marsden, the mylonising of the rocks along the major thrust plane,\* we would seem to have a proof that there must have been a considerable weight of rock over the area at the time of the action of these horizontal pressures.

The magnitude of the displacement produced by the thrusting at any particular point is difficult to determine as there is no case of a fault or other well-marked phenomenon being laterally displaced so that exact measurements could be made. There are two places at which the extent of the movement may be determined within broad limits. One is Marsden, where the amount of folding, etc., may be very roughly obtained, and a general estimate made of the crushing. The displacement here would appear to be about 300 feet. It should be noted, however, that the wide breccia-fissures on either side of the highly-folded area make the actual displacement of the whole strata very much less. The other place is at the Craggs, Hendon, south of Sunderland, where the Middle Limestone is thrust over the Upper for some distance (see Fig. 10). By obtaining as accurately as possible the amount of throw, which appears to be not less than 60 feet, and the hade, which is 75°, a rough

<sup>8</sup> See Section, fig. 8.

<sup>9</sup> Lebour and Smythe, *Q. J. G. S.*, vol. lxii., part 3 (Aug. 1906) pp. 530-551; and S. R. Haselhurst, *Univ. Durh. Phil. Soc.*, vol. 4, part 3 (1912), p. 162.

\* Can be best seen at Trow Rocks, South Shields (see photograph Fig. 11 in Memoir on Marsden).

computation of the displacement can be made. It appears to be about 250 feet. It is remarkable that such pronounced brecciation, etc., should be developed in the Permian with such apparently small horizontal displacements.

One of the peculiarities of the area is the juxtaposition of highly disturbed and undisturbed areas. The latter, however, are in many cases only apparently so, as there is no doubt that they have often moved, but the thrusting has been relieved by shearing and brecciation at particular points and its influence has not been propagated forward into the undisturbed masses.

While working on the Marsden section I endeavoured to obtain an estimate of the magnitude of the thrust by testing the compressive strengths of the series of rocks exposed in the section. It is the only place where this method could be adopted with any hope of success, as it is only here that a series of rocks have been driven against a Horst-like mass, and thus experiments made to determine the compressive strengths give an idea of the force required to produce brecciation. Dr. Morrow tested in the 100-ton testing machine of the Armstrong College Engineering Laboratory a series of specimens from this section, and the results obtained are given below. For a fuller description of this area reference should be made to my paper on the exposure at Marsden.<sup>10</sup> The results obtained appear to prove that the thrusting reached a maximum of some 300 tons per square foot. It is important to notice that as much solution and cementation has probably taken place in these rocks—much in the Brecciated Beds and less in the other strata—since they were brecciated, too much reliance cannot be placed on the results for giving a true estimate of the magnitude of the thrusting: the experiments, however, explain why certain rocks are shattered and others not, and also—from the sudden manner in which most of the specimens were fractured—indicate that during the time of thrusting a point would be reached in a particular rock when the whole mass would suddenly brecciate.

<sup>10</sup> *Op. jam. cit.*

COMPRESSIVE STRENGTHS OF THE CHIEF VARIETIES OF LIMESTONE  
EXPOSED IN THE SECTIONS.

TONS PER SQ. IN. TO BREAK THE ROCK TO PIECES.

A.	B.		C.
<p>Lower Limestone. Slightly folded and fissured, and the upper layers broken and sheared along the Major Thrust plane. Never brecciated.</p>	<p>Upper Middle and Lower Upper Limestones. 200 feet of variable rock folded, cleaved and dynamically brecciated against Horst and at sharp fold and along minor shear planes.</p>		<p>Brecciated Beds. Lower Middle. 50 to 60 feet thick, lying between A and B and almost entirely brecciated. The specimens tested were from the unbrecciated parts of these beds. The beds have been pushed along the Major Thrust plane lying along top of A.</p>
	<p>B<sub>1</sub> Main Mass.</p>	<p>B<sub>2</sub> A wedge-shaped mass of white limestone which is shattered against Horst.</p>	
4.9	2.2	1.4	0.6
8.4	2.3	1.4	1.3
4.1	3.7	2.5*	0.8
5.4	2.5	3.0*	1.1
	1.2		
Mean 5.7	2.2		0.9
<p>Clean fracture. Most rigid rock. Brittle rock.</p>	<p>Clean fracture. Rigid rock. Brittle rock.</p>	<p>Powdery fracture. Not so rigid. Brittle rock.</p>	<p>Very powdery fracture. Least rigid. Plastic rock.</p>

The specimens were selected by myself and placed in testing machine so that pressure was applied in the direction in which the thrusting took place. All the specimens were treated alike, being carefully trimmed and faced with a thin layer of plaster of Paris, and placed in the machine with four thicknesses of blotting paper on top and bottom, the spherical joint abutment being used to ensure an equal distribution of pressure.

\* These specimens were from the part of B<sub>2</sub> that had had cleavage structure impressed on it.

The direction of the thrusting may be inferred from certain observations. It is, however, of importance to notice that effects produced at any particular point may conceivably be caused by movements inclined at very considerable angles to the main direction of thrusting. The chief phenomena that may be used to determine the direction at any particular point are (1) cleavage (developed normal to the pressure), (2) slickensided and grooved planes, (3) the strike of the thrust planes, (4) the strike of the axes of folding and (5) the direction in which a particular bed, fault, etc., has been moved. Several observations of certain of these points have been made and doubtless many more will be noted and recorded from time to time.

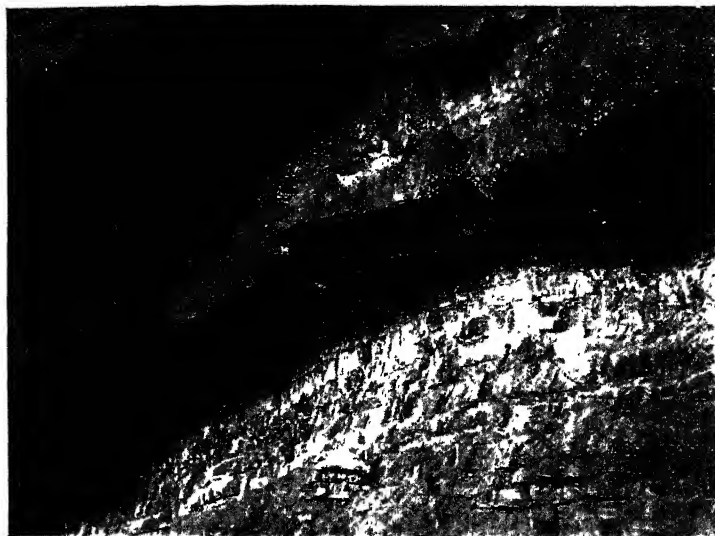
The three best areas in north-east Durham for obtaining the direction of the main pressures are Marsden, the coast south of Sunderland to Ryhope, and Claxheugh.

At Marsden cleavage is extensively developed. Its direction is  $10^{\circ}$  to  $15^{\circ}$  E. of N., and therefore the thrust here acted from  $10^{\circ}$  to  $15^{\circ}$  N. of W. and  $10^{\circ}$  to  $15^{\circ}$  S. of E. This highly cleaved area at Marsden was probably in equilibrium between the two forces, and it would seem that the best indication of the main direction of thrusting can be obtained here (Photograph, Fig. 16).

The strike of the thrust plane at the Craggs, Hendon, is as far as can be observed  $35^{\circ}$  S. of W. and its hade is  $75^{\circ}$  towards the south-east. The direction of movement of the Middle Limestone over the Upper was from  $35^{\circ}$  E. of S. (Fig. 10). At Jean Jiveson's rock strongly slickensided planes are developed in a mass of cleaved breccia. Their direction is  $30^{\circ}$  N. of E., and the direction of the thrusting was from  $30^{\circ}$  E. of S.

At Claxheugh there are several indications of the direction in which the upper beds have moved. In my description of Claxheugh I showed that the Yellow Sands were sheared at one point and dragged from the west up over a





*Photo by O. C. Walcott.*

FIG. 11.—REGULARLY-BEDDED LOWER LIMESTONE OVERLAIN BY THE  
MIDDLE UNBEDDED FOSSILIFEROUS LIMESTONE.

The base of the latter division is here distinctly grooved owing to the thrusting of it along the lower rocks. The direction of grooves is W.S.W. to E.N.E.—West-end of Claxheugh.



*Photo by O. C. Walcott.*

FIG. 12.—MAJOR THRUST PLANE  $T_1$  BETWEEN THE LOWER LIMESTONE L  
AND THE BRECCIATED BEDS B.

The disturbed beds D sheared along the thrust plane are here over 6 feet thick. A layer of mylonite occurs along  $T_1$ . Two sets of parallel fissures are seen to the left of the photograph.—Frenchman's Bay, South Shields.



mass of breccia several feet high.<sup>1</sup> An argillaceous bed that forms the base of the Marl Slate is slickensided along planes parallel and transverse to the bedding. The latter rise from west to east. Certain small folds are overfolded from west to east. The base of the Fossiliferous Middle Limestone is grooved, possibly by the lateral movement of this bed over the Lower Limestone (Fig. 11). Their direction is W.S.-W. to E.N.-E. ( $54^{\circ}$  Geog.), and from the other observations it may be inferred that the upper bed moved from the W.S.-W.

Some other local indications of the direction of movement have been observed. The base of a breccia lying in a minor thrust plane at Nose's Point (S. of Seaham Harbour) is slickensided from  $17^{\circ}$  E. of S. to  $17^{\circ}$  W. of N. The strike of the fold axes at Fulwell is roughly N. and S. and cleavage has been observed here, direction from  $10^{\circ}$  W. of N.

There is apparently no case of a fault having been displaced in a particular direction; and it is exceedingly difficult—except as already indicated in the case of the Yellow Sands at Claxheugh and the movement of the Middle over the Upper Limestone at Hendon—to determine the direction in which a particular bed has been moved.<sup>2</sup>

The thrusting discussed in this area appears to have been produced by a general movement of the strata (Permian and Coal Measures) and not by such minor internal movements as the conversion of beds of anhydrite into gypsum, and the major brecciated beds of this area are crush breccias and have not been formed by the solution of beds (*e.g.*, limestone, gypsum, etc.), and consequent collapse of caverns. It is, however, possible that all the brecciation in the Magnesian Limestone of Durham—even in the northern area—has not been produced by the same cause.

<sup>1</sup> See detailed section in paper on Claxheugh, *op. jam. cit.*, section 2, p. 211.

<sup>2</sup> A disturbance of considerable magnitude exists on the west side of Cleadon Hills, but its exact nature has not yet been deciphered.

The map, Fig. 13, shows the direction of the actual movement of the beds at places where it can be accurately obtained.

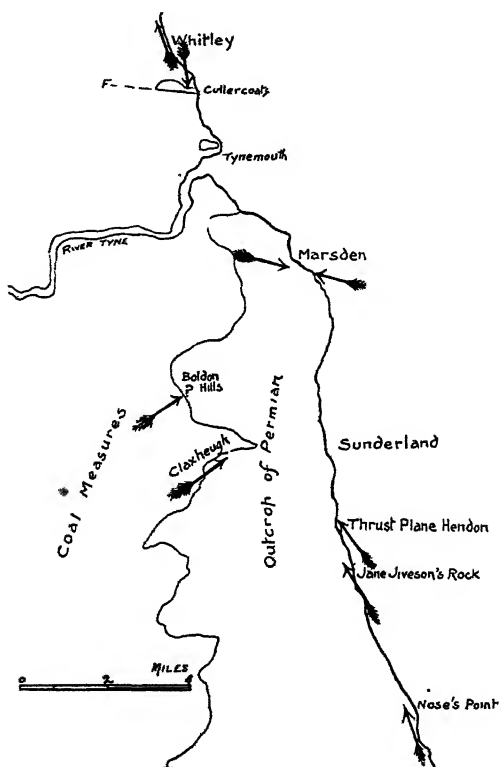


FIG. 13.

**MAP SHOWING DIRECTION OF THRUSTING AT DIFFERENT EXPOSURES, AS OBTAINED BY OBSERVATIONS ON SLICKENSIDED SURFACES, CLEAVAGES, ETC.**

Whitley, direction in Coal Measures as recorded by Lebour and Smythe (*Quart. Journ. Geol. Soc.*, vol. lxii., 1906).

Cullercoats, as stated by Haselhurst in paper on this area (*Univ. Durham Phil. Soc.* vol. iv. pp. 15-24).

Other observations made by author.

*Effects produced by the Thrusting.*

1. *Fractures*.—Fractures of many kinds and of very different magnitudes are found throughout the district. Some were not caused by the thrusting, but most of them were. Certain of the latter are characteristic of particular horizons.

(a) *Thrust planes* or *Shear planes*: These are more or less horizontal fractures along which the upper strata have been driven over those beneath, or they are fractures having at a considerable angle along which lower beds have been pushed over higher. They may be divided into major and minor according to the amount of horizontal displacement that has taken place along them. A major thrust plane occurs along the top of the Lower Limestone in all the northern parts of the district (Fig. 12). This fracture can be seen on Tynemouth Cliff, from Trow Rocks, South Shields, to Man Haven, on the flanks of Boldon Hills, at Claxheugh and probably on Chourndon Point to the south of Seaham Harbour. It probably underlies a large portion of the eastern district. The plane of demarcation between the Lower Limestone of high rigidity and compressive strength and the Middle rocks with these two properties very much less in magnitude has been the plane upon which the greatest horizontal movement has taken place. The Lower Limestone is often folded and fractured while the beds above are generally brecciated. The effects produced along this plane are the movement of large masses of the Lower Limestone out of position, and consequent fracturing, tilting and shearing of its upper beds. These disturbed beds were noticed by Howse,<sup>2</sup> but he thought they had been produced by denudation and denoted an unconformity,

<sup>2</sup> *Guide to Collection of Local Fossils in Museum of Nat. Hist. Soc., Newcastle* (1889), p. 10.

while Professor Lebour referred to their occurrence in Frenchman's Bay,<sup>3</sup> and considered that they might have been produced by thrusting. Another effect was the formation of a layer of mylonised rock in places along the thrust plane. The manner in which this bed an inch or two in thickness lies along the tilted edges of the disturbed strata is peculiar. It probably represents an original "mylonite" or ground rock, although it has undoubtedly undergone subsequent alteration. It may be looked upon as a kind of lubricating material. It is most distinctly developed along the coast between South Shields and Frenchman's Bay.<sup>4</sup> At one part it consists of minute hollow spheres, as if the original powder had been dissolved out and a more calcareous crystalline matrix left. At another place it consists of minute crystals of calcite. The grooving of the base of the Fossiliferous Limestone at Claxheugh was also probably produced by a horizontal movement of this bed. (Photograph, Fig. 11.)

Another major thrust plane occurs at the Craggs between Hendon and Ryhope (Fig. 10). This plane hades to the south-east at 75°. Here the yellow bedded Middle Limestone is thrust over the Flexible and lower Upper Limestone. Along this plane there has been a development of "phacoidal" structure,<sup>5</sup> and the beds overlying the fracture have been "block-fractured." The "phacoidal" structure (a kind of fracturing into ellipsoids) is a direct result of the shearing and a strain slip cleavage has also been produced.<sup>6</sup> It here affects some 15 to 20 feet of rock above the thrust plane (Fig. 14).

<sup>3</sup> In unpublished paper referred to on page 242.

<sup>4</sup> See photograph Fig. 11, Memoir on Marsden. *Op. jam. cit.*

<sup>5</sup> "Geological Structure of N.W. Highlands," *Mem. Geol. Sur.* (1907), pp. 149, 169, 263, 504, and photographs 224, 232.

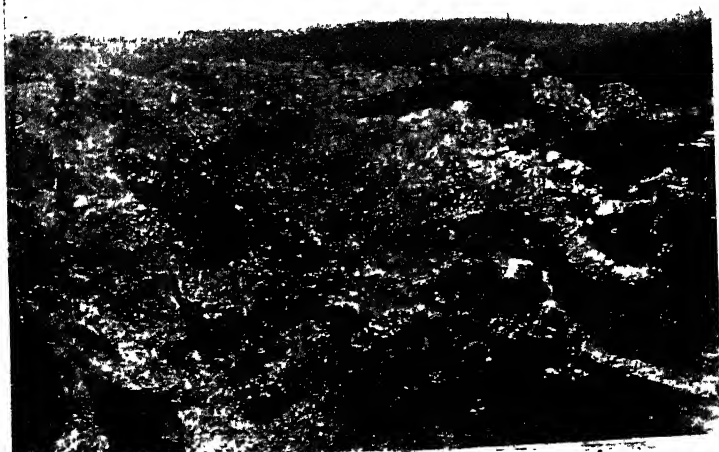
<sup>6</sup> This structure is similar to the megascopic pseudostromatolism described by Haselhurst in the Coal Measures at Whitley. *Op. jam. cit.*



*Photo by O. C. Wilmot.*

FIG. 14.—PHACOIDAL STRUCTURE PRODUCED BY SHEARING OF THE MIDDLE LIMESTONE ALONG THE THRUST PLANE AT THE CRAIG, HENDON, NEAR SUNDERLAND. (See Fig. 10.)

The rock is also block-fractured. The fractures were cemented and from some of these the cementing material has been removed and the fissures have been produced.



T.

*Photo by O. C. Wilmot*

FIG. 15.—FOLDING AND BUCKLING OF BEDS, SQUEEZING OUT OF SOFTER BEDS AND BRECCIATION OF ENTIRE MASS BY THRUSTING AGAINST IRREGULAR PLANE T P.

Base of Concretionary Limestone.—Marsden Bay, South of Grotto.





Minor thrust planes lying generally beneath brecciated beds occur at various horizons. They are as a rule more or less horizontal and are observable at the Marstack (of 1" maps), along cutting for colliery line near Ryhope, Featherbed rocks, Seaham Harbour and Nose's Point. The amount of displacement has generally been small.

(b) Besides these more or less horizontal fractures, numerous vertical and oblique fractures occur. A vertical fracture that runs for a third of a mile along the foreshore from Seaham Harbour southwards past Liddle Stack separates a highly brecciated from a non-brecciated area. The former region has moved relatively to the latter. Some of the parallel oblique fractures hade in a uniform direction, and others have polished surfaces and cleaved sides.

(c) Fracturing on a small scale also occurs. One of the most interesting cases of this is where the whole rock has been fractured into large irregular blocks. This type of structure, which is developed south of Marsden, and above the thrust plane at the Craggs, Hendon, I propose to call the "block fractured." (Figs. 10 and 14.) Sometimes the beds are minutely faulted, *e.g.*, in small quarry south of Claxheugh.

(d) The most widespread type of fracturing is the shattering of the rocks at various horizons into irregular masses and fragments—the Brecciated Beds, a full account of which is given on page 299.

2. As already explained the broad folding of the whole of the strata of the district is to a large extent due to the thrusting, as is also the local folding of the Lower and Upper Limestones. One of the marked features of the brecciated zone is, however, the small amount of folding occurring in it, indeed only the highly disturbed area to the

south of Marsden Bay (Fig. 9) can be called a contorted one. Occasionally the beds beneath a thrust plane are minutely folded (generally overfolded, thus indicating the direction in which the upper beds have moved). This has been observed at Claxheugh, Cullercoats, and Nose's Point.

3. Other effects which chiefly occur in the Marsden area are the buckling of beds, the squeezing out of the soft layers and the thickening of the harder, and the thrusting of beds into one another. The bulging out of beds is chiefly seen in the hard, grey, cleaved limestones, which have obviously taken most of the thrust, and the local thinning and thickening in the "marls" (Fig. 15).

4. A vertical cleavage structure has been impressed on the rock normal to the pressure at many points. It is also best developed in the Marsden area, where it has been produced subsequent to the folding and prior to the brecciation of the layer, as a folded rock is cut by vertical cleavage planes, and a cleaved rock can be seen to pass into a breccia. It is only developed here in the hard, grey limestones, not affecting the beds above or beneath them (Fig 16). Local cleavage occurs at several places in the district.

5. Another evidence of the pressure and consequent movement are the slickensided and grooved surfaces that occur at many points. They are best developed in the mass of intruded breccia of Jean Jiveson's rock (Fig. 10), but have also been observed in the breccia of the Marstack, beneath the breccia at Nose's Point, Seaham Harbour, and in a band of soft clay below the Marl Slate at Claxheugh and in Cullercoats Bay.

6. Some of the breccia-fissures and gashes and irregular brecciated masses that are so well exposed along the coast between South Shields and Sunderland appear to have been produced at the end of the period of thrusting.

## XIII.—CHARACTERISTICS OF THE BRECCIATED BEDS.

The bedded breccias in a continuous section vary in thickness from a hundred feet down to a few inches, and they are found at variable horizons through a stratigraphical range of about 400 feet. The size of the blocks varies from masses many hundreds of cubic feet down to the finest powder. The thick and widespread autoclastic rocks are almost entirely confined to the irregular deposits of the Middle Limestone and the lower part of the Upper Concretionary Limestone. They are traceable throughout the entire outcrop of these beds and can be followed southwards beyond the region of which this paper gives a detailed study. The chief exposures of them are (1) Marden Quarries near Whitley, (2) Tynemouth Cliff, (3) from Trow Rocks to the south of Marsden Bay, (4) Boldon Hills, (5) Quarries to the south of Claxheugh, (6) the banks of the Wear above and below Sunderland Bridge, (7) cutting for colliery line between Tunstall Hills and Ryhope, (8) Coast from Hendon to Hawthorn Hive, etc.

They have the following characteristics:—

(1.) The component fragments of the breccia are nearly always angular, and are composed of laminated and unbedded rocks. There does not appear to have been any production of a true "crush conglomerate" in the area, possibly proving that (except in certain cases where the breccia appears to have been cemented and then refractured) little movement took place after the first shattering of the rocks. Very occasionally rounded fragments occur but they seem to have been produced by subsequent solution. In some cases it may have been that the powder produced by intense fracturing may have prevented the rubbing of contiguous masses, but in general the movement subsequent to brecciation appears to have been slight. This would appear to indicate that during the time of thrusting a point was reached in many parts of the area at which the stress was

suddenly relieved by the brecciation of the mass, in a manner similar to the sudden fracturing of a block to which pressure is being applied in a testing machine.

(2.) In some cases the constituent fragments of the breccia are uncemented. This is especially the case with the hard, grey type of breccia, but sometimes the cementing material forms a large proportion of the rock. It would seem probable that in the case of the soft yellow rocks with a very powdery fracture the cementing material may have been produced by the shattering. The heat produced by the mechanical movements would increase the solvent power of the water contained in the strata, and as the powder would offer an enlarged surface, it would be largely dissolved and redeposited with a less quantity of magnesian carbonate than there was in the rock from which it was originally derived; thus the cementing material formed in this way may be hard, grey, crystalline and more calcareous than the fragments which it encloses. In other cases the cementing material would undoubtedly seem to have been infiltrated. It is noteworthy that the cement of the brecciated beds is generally hard, grey, more crystalline and more calcareous than the soft, yellow, marly cement of the breccia-gashes and breccia-fissures.

(3) The base, on which a thick autoclastic bed rests, is generally a disturbed one—it is either a major or minor thrust plane. In some cases, as to the north of Nose's Point, Seaham Harbour, the sole of the breccia is horizontally slickensided, while generally the beds beneath the thrust plane are minutely faulted and folded. Along the major thrust plane between the Lower and Middle Limestones in Frenchman's Bay and elsewhere, sheared and highly disturbed strata have been produced (Fig. 12).

(4.) The breccia has sometimes been indurated and rendered more calcareous and crystalline subsequent to its formation, so that parts of it may now be very different in colour, texture and composition from the beds from which it was originally derived.

(5.) In several parts of the brecciated areas the fragments have been dissolved out from the cementing matrix. This type of rock was called the "Pseudo-Brecciated" by King, and the "Cellular" or "Cavernous" by Sedgwick and Howse. Professor Lebour has suggested the term "negative-breccia." This structure forms one of the chief varieties of cellular rock in the Durham Permian. The holes are always angular. It would appear that where the fragments were composed of yellow Magnesian Limestone surrounded by a hard calcareous cement the pieces have been entirely, or in some cases only partly, dissolved. Recently (September, 1910) a bed of negative breccia derived from a shattered stratum of Concretionary Limestone was being worked in the Southwick Quarry of the Fulwell Lime Works, but it is a much more common structure in the Middle than in the other divisions. There is a type of negative breccia in which the holes are filled with soft, powdery marl, which would appear to have been introduced by subsequent infiltration.

(6.) While the chief breccias of the brecciated beds have been produced by thrusting, yet they have been brought about in various ways.

(a) Thrust- or shear-breccias produced by differential movement of contiguous beds—a smashing up of the rock caused by the frictional drag and shearing of the mass—*e.g.*, the Brecciated Beds above the major thrust plane in Frenchman's Bay, etc. (Fig. 9).

(b) Crush breccias caused by the direct crushing of the beds against a mass that stood as a Horst. This type is best developed in the south end of Marsden Bay (Fig. 15). The factors determining the amount of brecciation in this case would be the relative compressive strength, brittleness and rigidity of the rock (see page 291).

(c) Breccias have also been developed by flexure. Intense local folding of shattered rocks occurs at

Marsden south of the Grotto, and broken, unsymmetrical folds in the Concretionary Limestone in Fulwell Quarries.

(d) An induced cleavage structure has afterwards been developed into a brecciated rock by a slight differential movement of the mass. At Marsden a hard grey limestone has been first folded, then had a coarse cleavage structure developed in it, and later been irregularly shattered (Fig. 16).

(7.) The breccias have occasionally been intruded into the beds above. The best example of this is Jean Jiveson's rock (see Section Fig. 10), but there are several other local cases of breccias rising into disturbed beds, *e.g.*, banks of Wear west of Sunderland Bridge, Marsden Bay, etc.

In one case at least they appear to have been intruded also into the beds beneath. A grey breccia, which occurs among disturbed beds in an old quarry in a field to the east of the church at West Boldon, seems to be a breccia of the Middle Limestone pushed into the beds below, and it would seem possible that Kirkby was describing a similar disturbance in the Lower Limestone in Hartley's Quarry, Sunderland.<sup>6</sup>

(8.) Some of the breccias are cut by slickensided planes. They are best developed in the mass of intruded breccia at Jane Jiveson's rock, and a polished surface occurs in the breccia at the Marstack of 1" maps (Fig. 10).

(9.) At Jean Jiveson's rock the breccia is cleaved parallel to the slickensided planes (Fig. 10).

(10.) In some cases there would appear to have been two distinct movements. Cemented breccias (Boldon Hills, etc.) have been refractured into large cuboidal masses or horizontally arranged lenticles, or fissured. Also a very fine powdered breccia appears to have been cemented and then rebrecciated. It may be that cementation took place

<sup>6</sup> *Trans. Tyneside Nat. Field Club*, vol. vi., Part 2 (1864), p. 214.



*Photo by Godfrey B. Bingley.*

FIG. 16.—CLEAVAGE STRUCTURE PASSING INTO A BRECCIATED LIMESTONE.  
(Grey Crystalline Limestone, just above the Flexible Limestone.—  
Marsden Bay. South of Grotto.



*Photo by D. Woolacott.*

FIG. 17.—CELLULAR STRUCTURE PRODUCED IN SOFT YELLOW MAGNESIAN  
LIMESTONE BY LEACHING OUT OF THE MAGNESIAN CARBONATE.

The rock becomes whiter, more calcareous, crystalline and cellular.  
Middle Magnesian Limestone.—Hawthorn Limestone Quarry,  
near Seaham Harbour.





very shortly after the shattering (as it might do on hypothesis discussed in (2) on page 300), and thus the second fracturing into the large masses may not be separated from the first by a long interval.

(11.) Sometimes the fragments in the breccias are fossiliferous, and there is no doubt that in many cases the fossils have been obliterated, either by molecular changes in the fragments themselves or by the complete removal of them from the cementing matrix (negative breccia). Some of the chief brecciated beds, however, appear to have been formed from rocks that were originally unfossiliferous.

#### XIV.—FISSURES, BRECCIA-FISSURES, BRECCIA-GASHES, ETC.

The whole of the beds are more or less cut by fissures of various kinds. Some of these are vertical while many have in a particular direction, being in some areas both parallel in hade and direction. In some cases two parallel sets cross one another. Some of them are closed, some open reaching several inches across, while others are wide, measuring as much as 50 feet across and are filled with breccia that has fallen in from the beds above. Many of the closed fissures were undoubtedly caused by the thrusting, and the vertical breccia-fissures were produced at the end of the movements when the shattering took place. It is noteworthy that certain types of them are characteristic of particular horizons in the Permian. Along many of the closed fissures and fractures the rock has been rendered more calcareous.

They may be classified as follows:

(1) Fissures in the Yellow Sands. These are best developed at Cullercoats, where two sets of crossing parallel veins have been worked out by S. R. Haselhurst (see page 308), and at Claxheugh.

(2) Open vertical fissures or "backs" are found chiefly in the Lower Limestone, and are often seen cutting through the whole exposure of the rock (80 feet). They are best seen

at Houghton and in Hetton Downs Quarry. Their mode of origin is not quite clear, they do not afford any evidence of having been produced by the thrusting. Some of the wide open fissures filled with sand and gravel near Warden Law and Houghton-le-Spring would appear to be due to the washing out of the Yellow Sands from the limestone beneath.

A vertical fissure which occurs in the Fossiliferous Limestone on the north side of the southern hill at Tunstall is filled with hard cemented sand and along its sides the limestone has been rendered more calcareous, crystalline and concretionary.

(3) Many sloping fissures having in a certain direction and parallel to one another occur. There are sometimes two parallel sets cutting each other (Frenchman's Bay, Down Hill) and they appear to have been directly caused by the thrusting. Slickensided fissures occur, and south of Seaham Harbour some have cleaved sides.

(4) Vertical fissures with definite sides filled with breccia are exposed in the Marsden area. Some of them are 50 feet in width, and the blocks in them, which reach many hundreds of cubic feet in bulk, have sometimes fallen considerable distances (100 feet at least). Within the area no fragments from any other than the Permian have been found in them. It is proposed to call them "breccia-fissures." They occur on either side of the highly shattered area at Marsden, and would appear to have been produced at the end of the period of thrusting, when after the intense folding and brecciation took place, the strata of the horizon in which they occur crept in towards the shattered area.

(5) Breccia-gashes are typically triangular in section, and were first described by Professor Lebour.<sup>7</sup> That some of them may have been produced by the mechanical removal of beds of marl or by solution of beds is probable, but in the Marsden area many of them have resulted from movements in the limestone. It is difficult to distinguish these from irregular brecciated masses, which may sometimes have been

<sup>7</sup> *Op. jam. cit.*, p. 165.

caused by the removal of "marls," or may represent the tops of true breccia-gashes or breccia-fissures, or even of faults in the beds beneath.

The breccia in many of the fissures, gashes, etc., is cemented by a soft, earthy, yellow and highly magnesian matrix, which is quite different in character from the typical hard, grey calcareous one in which the fragments of the brecciated beds are enclosed.

### XV.—CELLULAR STRUCTURES

The Magnesian Limestone of Durham is a peculiarly cellular rock. It has been supposed by some geologists that these structures proved that the rock had been dolomitised subsequent to deposition; but it is noteworthy that the most cellular parts of the limestone are not the most magnesian; indeed most of the types of cellular structure appear to be due to the leaching out of the magnesium carbonate (in some cases indeed of both the calcium and magnesium carbonate) rather than to the decrease in volume (about  $\frac{1}{7}$ th) that would occur if the rock had been dolomitised subsequent to deposition. Whether the magnesium carbonate was originally always deposited along with the calcium carbonate, or whether the magnesia was introduced subsequent to deposition may be in some cases impossible of determination, but the fact seems clear that subsequent solution has led to the carrying away of the magnesium carbonate—dedolomitisation—and other impurities and the consequent production of a more calcareous, cellular rock—a purer limestone.<sup>1</sup>

The cellular structures that I have noticed may be divided into four or five district groups.

(1) *Concretionary-cellular* produced by the segregation of the calcium carbonate round points and along lines, and the removal of the earthy magnesian residue. This structure is almost entirely confined to the Concretionary Upper Lime-

<sup>1</sup> Under a pressure of 5 atmospheres magnesium carbonate is more soluble in water containing carbon dioxide than calcium carbonate; at atmospheric pressure the latter salt is the more soluble. Prof. Skeat's "Dolomites of "Southern Tyrol," *Quart. Journ. Geol. Soc.*, Feb. 1905, p. 135.

stone. Several types of concretionary structure may be included under this head—the honeycombed, coralloid, stellate, botryoidal, etc. Many of the “greystones” of the quarryman are cellular limestones of this type. (All parts of the Concretionary Limestone are not cellular, as there is sometimes a matrix round the concretions.)

(2) *Cellular or Negative-breccia*. This type has already been described on page 301. It is produced by the removal of the fragments of the yellow Magnesian Limestone breccia from the hard grey calcareous cementing matrix.

(3) *Solution-cavities* produced by the leaching out of the magnesium carbonate from a Magnesian Limestone and the production of a calcareous, crystalline, highly cellular rock. The most interesting and definite case of this occurs at Fox Cover Quarry, south of Seaham Harbour, where a highly fossiliferous, soft, yellow Magnesian Limestone has been changed into a hard crystalline rock full of cavities. The change is accompanied by a complete obliteration of the fossils. These alterations can be observed on a large scale, but hand specimens showing the whole of them can be obtained. We have here dedolomitisation accompanied with an obliteration of the fossil contents.

#### ANALYSIS OF LIMESTONE AT FOX COVER QUARRY, SEAHAM HARBOUR.

Yellow Fossiliferous Limestone.				Grey Crystalline Cellular Limestone (produced from the other).	
CaCO <sub>3</sub>	...	...	58·02	98·84	
MgCO <sub>3</sub>	...	...	38·33	·74	
SiO <sub>2</sub>	...	...	·35	1·	
Al <sub>2</sub> O <sub>3</sub>	...	...	·12	·12	
Fe <sub>2</sub> O <sub>3</sub>	...	...	·13	·18	

An analysis by R. C. Burton, B.Sc., of a hand specimen showing gradual obliteration of the fossils contained calcium and magnesium carbonate as follows:—

Yellow Fossiliferous.				Grey Crystalline Non-Fossiliferous.	
CaCO <sub>3</sub>	...	...	50·39	91·92	
MgCO <sub>3</sub>	...	...	40·93	8·01	

At Hawthorn Limestone Quarry (Fig. 17) further to the south a soft yellow limestone can be observed to pass into a

hard, grey, crystalline, cellular limestone, the chemical change being exactly similar to the last. A portion of the grey crystalline limestone has been partly silicified, being converted into a light-coloured banded cherty rock. The percentage of silica amounts to 39 per cent. Similar dedolomitisation has been observed at other places, *e.g.*, south of Easington Lane, Haswell, etc.

(4) *Geodes* are a cellular structure which are possibly connected in formation with the last type. They are typically developed in the Lower regularly-bedded limestone. They may be looked upon as being negative concretions, but it is not clear what the original chemical constituents of the geodes were. These cells are generally lined with crystals of dolomite and calcite, and sometimes with chalybite and ankerite.

(5) *Fractured-cellular*. This type is peculiar to the brecciated zone and is best developed on the coast to the south of Seaham Harbour. The rock has been fractured into rhomboidal masses, and these fractures have been cemented by calcareous matter, and the rock on either side rendered more calcareous. The yellow Magnesian Limestone has afterwards been removed to produce a cellular rock, some of the cells being several cubic feet in size, while others are quite small. An analysis of a piece of limestone between the fractures from the coast south of Seaham Harbour gives  $\text{CaCO}_3$  57.8 per cent.,  $\text{MgCO}_3$  39.2, while along the fractures the percentage of  $\text{CaCO}_3$  is 85.9 per cent. and  $\text{MgCO}_3$  8.19.

It is important to notice that changes in the composition of the limestone appear also to have been produced without an accompanying production of cellular structures, and it would seem incorrect to definitely assert that none of the irregular cellular and porous varieties of the limestone may not have been produced by a dolomitisation of that part, but the most cellular types certainly seem to have been formed by a removal of the magnesium carbonate or in some cases of both the constituent carbonates from the rock.

## XVI.—THE PERMIAN OF NORTHUMBERLAND.

(In collaboration with S. R. Haselhurst, M.Sc.)

(See section fig. 8, page 266)

The Permian system in Northumberland is developed in four outliers at Closing Hill near Killingworth, at Hartley, in Cullercoats Bay and Marden Quarry, Whitley and at Tynemouth. The Yellow Sands were exposed at Closing Hill on the north or down-throw side of the Ninety Fathom Dyke many years ago and have been noticed by Hutton<sup>8</sup> and Lebour,<sup>9</sup> but they are not now visible. The exposure at Hartley is also of this deposit only. At the other places the Marl Slate, Lower Limestones and Middle Breccias are developed as well as the Yellow Sands, and as the beds offer distinct stratigraphical peculiarities, besides affording evidence of the age and nature of the thrusting to which the district has been subjected, they are of special interest. In Cullercoats Bay the Permian has been let down on the north-side of the Ninety Fathom "Dyke," while on Tynemouth Cliff it exists as an outlier produced by denudation (Fig. 8). The stratigraphical peculiarities of the Tynemouth section are that a calcareous sandstone and conglomerate with rounded grains of quartz and other mineral and rock fragments, and characterised by ferruginous nodules and encrinite stems (*rémanié*) occurs between the Marl Slate and Lower bedded limestones. This siliceous bed passes laterally into a limestone. Early descriptions of Tynemouth place the Marl Slate among the Lower Limestones in an exceptional horizon<sup>10</sup> or say it is absent,<sup>11</sup> but there can be no doubt that here it rests in its usual place on the top of the Yellow Sands. It is dark grey, and S. R. Haselhurst has found scales of *Acrolepis* and *Palæoniscus* in it. The Brecciated Limestone on the top of the cliff is probably a brecciated part of the

<sup>8</sup> *Op. jam. cit.*, p. 72.<sup>9</sup> *Geology of Northumberland and Durham* (1889), p. 35.<sup>10</sup> Sedgwick, *op. jam. cit.*, plate vi., fig. i. Lebour, *ibid.*, p. 35 and section.<sup>11</sup> King, *op jam. cit.* p. 11.

Fossiliferous Middle Limestone, as King records 21 species from fragments of rock in the breccia.<sup>2</sup> In Cullercoats Bay some beds of sand similar in character to the Yellow Sands are intercalated in the lower beds of the limestone above the Marl Slate. The Lower Limestone in Marden Quarry, which is now covered by water, was very fossiliferous. Kirkby records 11 species.<sup>3</sup>

The structural features of the two areas afford a means of linking up phenomena on the north side of the Tyne with that on the south. The major thrust plane between the Middle Breccias and the Lower Limestone in Frenchman's Bay is developed on Tynemouth Cliff with the Disturbed Beds beneath it and the breccia and negative breccia above. The Disturbed Beds are also exposed in Cullercoats Bay and the Brecciated Limestone above in the Marden Quarry. S. R. Haselhurst has brought forward evidence to show that the Cullercoats area is a denuded dome, developed by thrusting of the Permian rocks from the north-west against the Coal Measures—which acted as a Horst—on the south side of the Ninety Fathom Dyke. He thinks, that as in other areas where the Yellow Sands are faulted, a series of parallel veins or slip planes—running N. 63° W.—would be produced in the Yellow Sands by the Post-Permian movement of the Ninety Fathom fault and that these veins when the thrusting occurred were developed into a series of crush veins. The veins are cut at 60° by a parallel set of oblique shear planes (direction a few degrees W. of N.), and they appear as a series of parallel fractures in the Lower Limestone. The limestone is altered along them into a more calcareous rock. Movement has also taken place along the crush veins as the shear planes are faulted by them, being shifted towards the east. There is also a considerable amount of faulting—often reversed—in the Sands of this area. The thrusting has also slickensided

<sup>2</sup> *Op. jam. cit.*, p. 11.

<sup>3</sup> "On the Fossils of the Marl Slate and Lower Limestone," *Nat. Hist. Trans. North. and Dur.*, vol. i., Part 2 (1866), p. 188.

the Marl Slate both along the bedding and transverse to it, and has folded the whole of the series into an irregular anti-

THE SERIES EXPOSED IN THE PERMIAN OUTLIERS OF NORTHUMBERLAND.

	Tynemouth Cliff		Cullercoats Bay	Marden Quarry, Whitley.	Hartley.
	Section a. Facing east South end of cliff.	Section b. Facing north east North end of cliff	Section c.	Section d.	Section e.
1	Brecciated Cellular Middle Limestone 18'-20'	Brecciated Cellular Middle Limestone 10'-15'		Brecciated Limestone 15'-18' Band of heavy spar	
2	Thrust plane	Thrust plane		Thrust plane	
3	Bedded Limestone 5' (disturbed) An arenaceous limestone with ferruginous nodules, encrinite stems 6'+	A series of alternations of marls, limestones, sandstones, regularly stratified and little disturbed 18'	Disturbed Lower Limestone 8'-10' Bedded Limestone with vein of heavy spar and galena Thin beds of sand near base 6'	Bedded Limestone slickensided 20'	
4	Marl Slate with <i>Acrolepis</i> scales 3' Yellow Clay puckered and slickensided 3'	Marl Slate with <i>Palæoniscus</i> 3'	Marl Slate with <i>Pygopterus</i> , <i>Acrolepis</i> , <i>Palæoniscus</i> , <i>Cœlacanthus</i> , slickensided along laminæ 3' three alternations of white sand, yellow clay and black shale 1'	Marl Slate 3' 6"	
5	White Sand 1' Reddish Sands 3' Yellow Sands with crush veins, minor faults, and false bedding 20'-22'	Yellow Sands 1' Magnesian Limestone 6' Yellow Sands 1' 6" Yellow Marl 1' Red Marl 1'	Red iron stained Sand 6' Yellow Sands with strongly marked crush veins and minor faults 70'	Yellow Sands?	Red Sand? Yellow Sands with veins and minor faults 20'-25' Red Sands 6' White Clay with large quartz pebbles 3'

Rest unconformably on Coal Measures.

cline. As the highly compressible Yellow Sands, probably already fissured parallel to the Fault, have been rather



crushed and squeezed than folded, and the Lower Limestones have not easily accommodated themselves to this, the dome is fractured and of a sharp and unsymmetrical nature. The area appears to prove that the thrusting took place subsequent to the Post-Permian movement of the Ninety Fathom "Dyke."<sup>4</sup> It is of interest that there are many evidences of thrusting in the Coal Measures of the Tynemouth, Cullercoats and Whitley<sup>5</sup> areas.

#### XVII.—RELATION OF THE PHENOMENA TO THE GENERAL GEOLOGY OF THE DISTRICT.

Some conclusions of local and general geological interest may be drawn from the different aspects of the Permian discussed in this paper. A brief summary of the more important of these is here given.

(1) That the Coal Measures of Northumberland and Durham were folded into a basin, and were considerably faulted and denuded before the Permian rocks were deposited on them.

(2) That the Yellow Sands were originally an æolian deposit.

(3) That the Marl Slate, Magnesian Limestone and Upper red beds with salt, etc., are the results of deposition in a more or less isolated sea cut off from the west of England by the Pennine anticline and spreading far to the east of the present outcrop of the Permian rocks.

(4) That the magnesium salts were originally present in the Permian Sea, and that the magnesium may have introduced into the limestone during or immediately after deposition by the action of magnesium chloride on the calcium carbonate.

<sup>4</sup> For a fuller account of the Permian of the Cullercoats and Tynemouth areas, see S. R. Haselhurst, *Proc. Univ. Dur. Phil. Soc.*, vol. iv., Part 1 (1911), pp. 15-24.

<sup>5</sup> Lebour and Smythe, *op. jam. cit.*, and S. R. Haselhurst "On a case of megascopic pseudo-stromatolism in the Coal Measures of Northumberland," *ibid.*, vol. iv., Part 3, p. 162.

(5) That considerable changes in the distribution and amounts of both the calcium and magnesium carbonates—but more especially of the latter—has taken place since deposition.

(6) That the chief types of concretionary structure were probably started after the deposition of the beds by the segregation of the calcium carbonate and leaching out of the magnesium carbonate from an impure magnesian limestone of intermediate composition.

(7) That the chief cellular structures in the limestone appear to be chiefly due to the leaching out of magnesium carbonate and segregation of the calcium carbonate (in some cases both carbonates have been removed) and have not been produced by dolomitisation.

(8) That in the north-east of Durham the major Brecciated Beds and associated phenomena are the result of thrusting, and that this thrusting also accentuated the syncline of the Coal Measures and folded the Permian of the area.

(9) That the main direction of thrusting as obtained in the Marsden area appears to have been from a few degrees North of West and a few degrees South of East, but motion of the strata from other points of the compass took place at other places.

(10) That it is exceedingly difficult to fix the age of these disturbances, but the phenomena in Cullercoats Bay appear to have been produced later than the Post-Permian movement of the Ninety Fathom "Dyke" (which is possibly of the same age as the later movements of the Pennine Fault and Vale of Pickering Fault and therefore probably at the end of the Cretaceous Period). From other considerations it may be inferred that the thrusting took place prior to the commencement of the pre-glacial era of denudation—that is in Miocene times.

(11) That some faulting in the Permian has taken place since the thrusting, *e.g.*, fault at east end of Claxheugh, fault in Marsden Bay, fault in Tynemouth Cliff, etc.

(12) That the thrusting is probably connected with some general movement of the North of England strata, and it is possible, as suggested by Garwood, that it occurred synchronously with the Post-Permian movements along the west of the Pennine Chain against the great "Horst" of the Lake District massif.<sup>6</sup> It seems, however, rather premature to generalise until more detailed work has been done on the North of England rocks from the tectonic point of view. Marr has endeavoured to show that the Lake District dome was formed in the Miocene period,<sup>7</sup> and it may be that the thrusting, the effects of which are observable in the Permian of Northumberland and Durham, is one of the phenomena connected with the Miocene uplift which produced such marked changes in the Physiography of Britain.

In conclusion I desire to thank Professor Lebour and Dr. Smythe for suggestions, advice and criticism; Dr. Morrow for testing the series of specimens from Marsden; S. R. Haselhurst and C. T. Trechmann for aiding me in the preparation of certain parts of the paper; O. C. Wilmot and Godfrey Bingley for taking photographs illustrating the phenomena of the area; and several graduates of Armstrong College for analysing specimens, aiding in the working out of sections, etc., viz., E. Merrick, R. C. Burton, S. Robson, F. H. Walker, G. Weyman.

<sup>6</sup> Garwood, "Geology of Northumberland and Durham, Geology in the Field," Geol. Assoc. (1910), p. 664.

<sup>7</sup> Marr, Presidential Address to the Geol. Soc., vol. 62, May, 1906, p. lxxvii.



# Financial Report for Session 1911-12.

## General Revenue Account.

INCOME.		EXPENDITURE.	
	£ s. d.		£ s. d.
Balance brought forward	...	Transferred to reserve	...
Bank Interest	...	Stationery, etc.	...
Sale of Proceedings	...	Postage	...
Sale of Memoir	...	Clerical, etc.	...
Grant from Armstrong College	...	Cost of Authors' Reprints	...
Sale of Authors' Reprints	...	Printing Proceedings:—	...
Annual Subscriptions:—	...	Vol. IV., Pt. 3	£28 8 4
1 for 1909-1910	£0 5 0	Vol. IV., Pt. 4	22 14 3
4 for 1910-11	1 10 0		...
94 at 10/- } 1911-12	54 10 0	Balance in hand	...
30 at 5/- }	...		51 2 7
7 for 1912-13	3 0 0		20 4 9
	59 5 0		...
	<u>£111 16 8</u>		<u>£111 16 8</u>

### Reserve Fund.

	£ s. d.		£ s. d.
Balance brought forward	...	Balance in fund	...
Transfer from revenue	...		57 5 6
	...		<u>£57 5 6</u>
	<u>£57 5 6</u>		
<b>Life Composition Fund.</b>			
6 Composition Fees	...	Balance in fund	...
	...		£30 0 0
	...		<u>£30 0 0</u>

T. H. HAVELOCK,  
Hon. Treasurer.

Audited and found correct,  
C. M. JESSOP.  
November 15th, 1912.



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